PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 18 May 2001 (18.05.01)	
International application No. PCT/KR00/00922	**Applicant's or agent's file reference** 00PCT-09JK
International filing date (day/month/year) 18 August 2000 (18.08.00)	**Priority date** (day/month/year) 19 August 1999 (19.08.99)
Applicant JUNG, Kweon	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

08 February 2001 (08.02.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Olivia TEFY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
00PCT-09JK		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/KR00/00922	18 AUGUST 2000 (18.08.2000)	19 AUGUST 1999 (19.08.1999)
Applicant		
JUNG, Kweon et al		

This International search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
   ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:
   ☐ contained in the international application in written form.
   ☐ filed together with the international application in computer readable form.
   ☐ furnished subsequently to this Authority in written form.
   ☐ furnished subsequently to this Authority in computer readable form.
   ☐ the statement that the subsequenlty furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (See Box II).

4. With regard to the **title,**
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawing** to be published with the abstract is Figure No. 6
   ☒ as suggested by the applicant.
   ☐ None of the figures.
   ☐ because the applicant failed to suggest a figure.
   ☐ because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/00922

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C02F 11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)
IPC7 C02F A62D 3/00

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched
Korean Patents and applications for inventions since 1975
Korean Utility models and applications for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search trerms used)
NPS, IPN, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95/022375 A1 (ECCLES, Harry) 24 August 1995 see the whole document,	1- 8
A	KR 1998-67148 A (Korea Institute of Science and Technology) 15 October 1998 see the whole document,	1- 8
A	US 4,354,937 A (Vyrmetoder AB) 19 October 1982 see the whole document,	1- 8
A	US 4,522,723 A (Kerr-McGee Corporation) 11 June 1985 see the whole document,	1- 8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevence
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevence; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevence; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 DECEMBER 2000 (08.12.2000)	09 DECEMBER 2000 (09.12.2000)

Name and mailing address of the ISA/KR	Authorized officer
Korean Industrial Property Office Government Complex-Taejon, Dunsan-dong, So-ku, Taejon Metropolitan City 302-701, Republic of Korea Facsimile No. 82-42-472-7140	WON, Jong Hyeok Telephone No. 82-42-481-5703

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR00/00922

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 95/022375 A1	24. 08. 95	RU2133632C1	27.07.99
		JP9522375 W1	24.08.95
		EP744982 A1	04.12.96
		US5840191 A	11.24.98
KR 1998-67148 A	15.10.98	None	
US 4,354,937 A	19.10.82	None	
US 4,522,723 A	11.06.85	None	

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Artcle 36 and Rule 70)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. **PCT/KR00/00922**	International filing date *(day/month/year)* 18 AUGUST 2000 (18.08.2000)	Priority date *(day/month/year)* 19 AUGUST 1999 (19.08.1999)

International Patent Classification (IPC) or national classification and IPC

IPC7 C02F 11/02

Applicant

JUNG, Kweon et al

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demamd	Date of completion of this report
08 FEBRUARY 2001 (08.02.2001)	21 DECEMBER 2001 (21.12.2001)

Name and mailing address of the IPEA/KR
Korean Intellectual Property Office
Government Complex-Daejeon, Dunsan-dong, Seo-gu, Daejeon Metropolitan City 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
LEE, Su Hyoung
Telephone No. 82-42-481-5597

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International aplication No.
PCT/KR00/00922

I. Basis of the report

1. With regard to the elements of the international application:*

[X] the international application as originally filed

[X] the description:
pages 1 - 18 , as originally filed
pages _____ , filed with the demand
pages _____ , filed with the letter of _____

[X] the claims:
pages 19 - 21 , as originally filed
pages _____ , as amended (together with any statment) under Article 19
pages _____ , filed with the demand
pages _____ , filed with the letter of _____

[X] the drawings:
pages 23 - 30, Fig 1 - 8 , as originally filed
pages _____ , filed with the demand
pages _____ , filed with the letter of _____

[ ] the sequence listing part of the description:
pages _____ , as originally filed
pages _____ , filed with the demand
pages _____ , filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application(under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination(under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide** and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

[ ] contained inthe international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disc losure in the international applicationas as filed has been furinshed.

[ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. [ ] The amendments have resulted in the cancellation of:

[ ] the description, pages _____

[ ] the claims, Nos. _____

[ ] the drawings, sheet _____

5. [ ] This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box(Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed." and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International aplication No.
PCT/KR00/00922

V. **Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1 - 8	YES
	Claims		NO
Inventive step (IS)	Claims	1 - 8	YES
	Claims		NO
Industrial applicability (IA)	Claims	1 - 8	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

1. The following documents identified in the International Search Report have been considered for the purpose of this report:

D1 - WO 95/22375 A1
D2 - KR 98-067148 A
D3 - US 4,354,937 A
D4 - US 4,522,723 A

2. The present application relates to a method of treating the incineration ash containing the heavy metals and the organic wastes containing the wastewater sludge and sulfate-reducing bacteria by burying them together under the ground(claims 1 to 2), and by further covering them with a depth of soil(claims 3 to 5), and by treating the aqueous elutes exuding out of the incineration ash and organic wastes containing the said sulfate-reducing bacteria in a disposal plant(claims 6 to 8).

Claims 1 to 2 relate to a method of burying the incineration ash containing the heavy metal together with the organic wastes containing the wastewater sludge and sulfate-reducing bacteria under the ground.

Claims 3 to 5 relate to a method of burying the incineration ash containing the heavy metals together with the organic wastes containing the wastewater sludge and sulfate-reducing bacteria under the ground, and further covering them with a depth of soil.

WO 01/14261
PCT/KR00/00922

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:
YANG, Soon-Seok
Durey Patent Office
#401, Kangnam-Jeil Building
822-4 Yoksam-dong
Kangnam-ku
Seoul 135-080
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year)	
01 March 2001 (01.03.01)	
Applicant's or agent's file reference	**IMPORTANT NOTICE**
00PCT-09JK	

International application No.	International filing date (day/month/year)	Priority date (day/month/year)
PCT/KR00/00922	18 August 2000 (18.08.00)	19 August 1999 (19.08.99)

Applicant
JUNG, Kweon et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   EP,JP

   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
   01 March 2001 (01.03.01) under No. WO 01/14261

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, **a demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer
J. Zahra

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREA

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

YANG, Soon-Seok
Durey Patent Office
#401, Kangnam-jeil Building
822-4 Yoksam-dong
Kangnam-ku
Seoul 135-080
RÉPUBLIQUE DE CORÉE

Date of mailing (day/month/year) 28 September 2000 (28.09.00)	
Applicant's or agent's file reference 00PCT-09JK	**IMPORTANT NOTIFICATION**
International application No. PCT/KR00/00922	International filing date (day/month/year) 18 August 2000 (18.08.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 19 August 1999 (19.08.99)
Applicant JUNG, Kweon et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.

3. An **asterisk(*)** appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

4. The **letters "NR"** appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 Augu 1999 (19.08.99)	1999/34333	KR	13 Sept 2000 (13.09.00)

The International Bureau of WIPO
34, chemin des Col mbettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Anman QIU

Telephone No. (41-22) 338.83.38

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number
WO 01/14261 A1

(51) International Patent Classification[7]: C02F 11/02

(21) International Application Number: PCT/KR00/00922

(22) International Filing Date: 18 August 2000 (18.08.2000)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
1999/34333 19 August 1999 (19.08.1999) KR

(71) Applicants *(for all designated States except US)*: **SHIN, Jai-Young** [KR/KR]; #Ra-1205, Sora Apt., Pangbae-dong, Seocho-ku, Seoul 137-060 (KR). **KIM, Min-Young** [KR/KR]; 288-1 Kyohyon-ri, Changheung-myon, Yangju-kun, Kyonggi-do 482-810 (KR).

(71) Applicant and
(72) Inventor: **JUNG, Kweon** [KR/KR]; #1316-1601, Tongbaek Apt., Sanbon-dong, Kunpo-shi, Kyonggi-do 435-040 (KR).

(74) Agent: YANG, Soon-Seok; Durey Patent Office, #401, Kangnam-Jeil Building 822-4 Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).

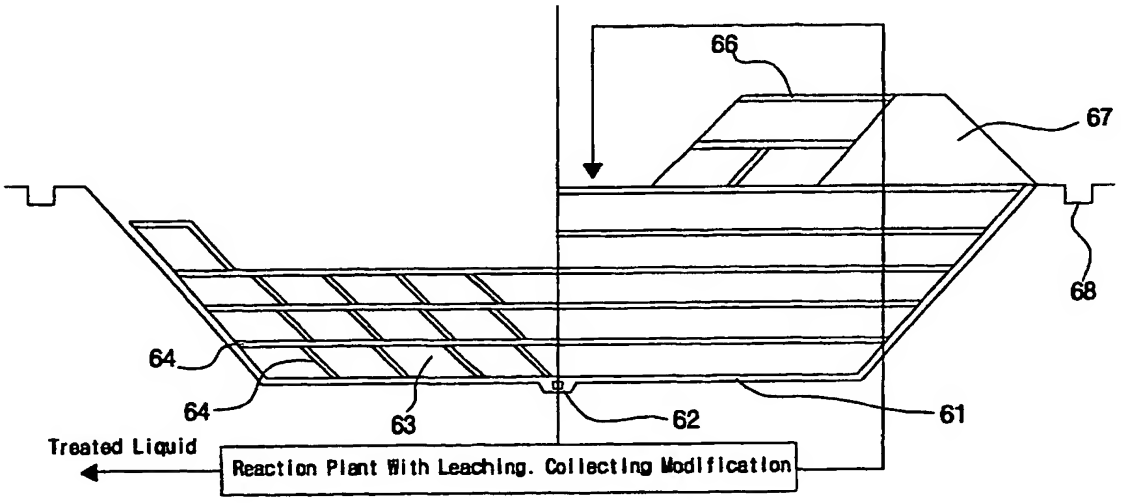
(81) Designated States *(national)*: JP, US.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF TREATING INCINERATION ASHES WITH SULFATE REDUCING BACTERIA



(57) Abstract: The present invention relates to a method of treating the incineration ash containing the heavy metal and the wastewater sludge by making the heavy metals existing in the incineration ashes insolulable, and separating from the ashes, then burying them in the conventional structure used for burying the plants, such that the present invention will bring the advantages of securing the region used for the landfills with lower costs.

WO 01/14261 A1

METHOD OF TREATING INCINERATION ASHES WITH SULFATE REDUCING BACTERIA

Technical Field

The present invention relates to a method of treating the incineration ash containing the heavy metal and the wastewater sludge, and more particularly, to a method comprising the steps of making the heavy metals existing in the incineration ashes insolulable, stabilizing the organic materials and separating from the ashes, and burying them in the conventional structure used for burying the plants. And such process is based on the reasonable plan considering the mutual relations between the properties.

Background Art

The method of disposing the solid wastes recently causes an additional problem of city life since the method depends mainly on burying them under the ground. However, it is scarcely possible to secure a vast area of ground enough to bury the wastes even in the countries having the small territory in area such as Korea. Therefore, as an alternative plan, a method of treating the wastes by combusting them has been proposed for extending the effective life of the ground to bury in.

In case that the wastes are incinerated and buried in the ground, an advantage that the effective life of landfill may be extended by reducing the volume of trash to be buried may be achieved.

Generally, there have been proposed two types of methods of treating the incineration ash, one of which is the conventional solidification method carried out by mixing the solidifier and the incineration ash together with the additional water in a mixer,

and then solidifying the mixture. And a chemical method of solid stabilization by adding a certain chemical agent to the incineration ash to stabilize the heavy metals existing in the ash.

However, the conventional solidification method has several defects as follows:

1) The effect of reducing the volume of incineration ash is not significant, 2) since the heavy metal in the cement may be eluded out depending pH value, the possibility of elution of the heavy metal is great, and 3) the cost for treatment is also high. The chemical method also has the defects that: 1) the expensive chemicals (chelating agents) should be used; 2) another possible problem causing another contamination may be caused due to using those chemicals (chelating agents); and 3) the possibility of elution of the heavy metal depending on pH is still high.

It is shown in the Fig.1 and 2 attached herein that the defects of the prior art, depict the amount of heavy metal contained in the incineration ash and the amount of elution, respectively. And Fig. 2 shows the result of elution test carried out by TCLP method.

Fig. 1 shows the amount of total contents of heavy metal, which the heavy metal contained in the incineration ash comprises 15.936 mg/kg of Pb, 620 mg/kg of Cd, 1.662 mg/kg of Cu, 20.311 mg/kg of Zn and so forth, which is relatively great amount.

Furthermore, as a result of analyzing the elements of incineration ash, it was detected that the incineration ash contained little nitrogen (N) and up to 3.997% of sulfur.

Fig.2 shows the amount of elution of heavy metal, which the heavy metal eluded from the incineration ash comprises 12.51 mg/l of Pb, 17.03 mg/l of Cd, 5.90 mg/l of Cu, 302.19 mg/l of Zn etc., which significantly exceeds the current standard allowed by the government.

As mentioned above, a little amounts of heavy metals incinerated is not essentially

removed from the ash during the incineration process but it is just being concentrated and still existing in the incinerated ash (as being the fly ash as well as the ash lain on the bottom). And if entrapped by the dust collector, its concentration becomes much higher than that has not gone through the incineration. The heavy metals contained in the fly ash and the ash lain on the bottom may be eluded by the rain water when filled in the landfill, and become the leachate, which may cause the secondary contamination of soil and underground water. Therefore, a suitable control and/or treatment are required in order to avoid such contamination.

Disclosure of Invention

It is therefore the object of the present invention to provide an essential method for treatment of the incineration ash, which may solve above problems.

The present invention provides a method of treating the incineration ash and the wastewater sludge (hereinafter, called as "incineration ash"), both of which contain a certain amounts of heavy metals, which comprises the steps of converting the heavy metals contained in the incineration ash into an insoluble state, using a safe manner, in order to prevent the exuding of the heavy metals from the incineration ash outwardly when eluded.

The present invention also provides a method for treatment of the incineration ash by burying together with together with organic wastes, which comprises treating the incineration ash with sulfate-reducing bacteria, which may be provided by the organic wastes containing the sulfate-reducing bacteria.

To accomplish above object, the present invention provides a method for treatment of the incineration ash and the wastewater sludge, wherein a mutual relation in using

nutrients exists between the incineration ash containing the heavy metal and the organic wastes containing the wastewater sludge and sulfate-reducing bacteria, which comprises: burying the incineration ash together with the organic wastes under the ground, in which the bacteria reduce the sulfates existing in the incineration ash to form the sulfides, and binding the formed sulfides with the heavy metal to form the insoluble metal sulfides, in order to prevent the heavy metal from exuding out of the incineration ash as eluate.

The present invention also provides a method for treatment of the incineration ash and the wastewater sludge, comprising: burying the incineration ash together with the organic wastes containing the sulfate-reducing bacteria under the ground, and covering them with a depth of soil, so that the said sulfate-reducing bacteria promote the heavy metal to precipitate in the form of insoluble metal sulfides, in order to prevent the heavy metal from exuding out of the incineration ash as eluate.

The present invention further provides a method for treatment of the incineration ash and the wastewater sludge, which comprises: collecting and mixing the aqueous eluate exuding out of the incineration ash and the aqueous eluate exuding out of the organic waste containing the said sulfate-reducing bacteria in a disposal plant, and reacting both the aqueous eluates so that the said sulfate-reducing bacteria existing in the aqueous eluate exuding out of the organic waste deposits the heavy metals from the aqueous eluate exuding out of the incineration ash as the insoluble metal sulfides, resulting in the disposal of the aqueous eluate exuding out of the incineration ash and the aqueous eluate exuding out of the organic waste.

Furthermore, according to an aspect of the invention, the said organic wastes may comprise the sewage sludge containing the said sulfate-reducing bacteria.

The present invention will be described hereinafter by referring to attached

drawings.

The present invention provides a method for treatment of the incineration ash and the wastewater sludge, which is carried out by reducing the large amount of sulfates in the inclination ash into the sulfides, binding the sulfides with the heavy metals from the inclination ash, and precipitating and removing the insoluble metal sulfides as formed.

Fig. 3 shows the result of analysis for the elements of the incineration ash by use of element analyzer. As seen from the Fig.3, a large amount of sulfur element exists in the incineration ash.

The element sulfur binds with oxygen in the incineration ash, and exists in the form of sulfate (SO_4^{-2}) in the solution containing the incineration ash.

The mechanism of binding the heavy metal with sulfur in the incineration ash by the sulfate-reducing bacteria will be explained hereinafter referring to Fig. 4.

Fig. 4 shows the pathway through which the sulfate (SO_4^{-2}) is to be reduced into sulfides (S^{-2}) by the sulfate-reducing bacteria.

The sulfate (SO_4^{-2}) in the incineration ash is reduced to the sulfides (S^{-2}) by the sulfate-reducing bacteria, and the sulfides bind to the elemental heavy metal to form the precipitate including the insoluble metal sulfides.

In general, the sulfate-reducing bacterium is a kind of anaerobic bacterium, and produces the energy by utilizing lactic acids, resulting in the formation of acetic acid and so forth as the metabolic products. According to this manner, the sulfate-reducing bacteria reduce the sulfates through the anabolic pathway for decomposition of organic compounds.

Furthermore, the sulfate-reducing bacteria can also decompose fatty acids such as palmitic acid as well as the aromatic compounds such as benzoic acid or phenol.

A variety of the sulfate-reducing bacteria existing in the ecosystem on earth require a large amount of energy for decomposing the stable salt such as sulfate (SO_4^{-2}), and take its role as the final decomposer of the organic compounds likely the methane bacterium in the ecosystem.

In other words, the sulfate-reducing bacteria reduce the sulfate (SO_4^{-2}) as being the inorganic compound, which acts as the electron receptor under the anaerobic condition in the biological environment, to the sulfides (S^{-2}, HS or H_2S), wherein the organic compounds as being used as the electron donor are oxidized. And, the formed sulfides (S^{-2}, HS or H_2S) and the heavy metal in the incineration ash bind together due to having the attraction between them, and precipitated.

Since the metal sulfides formed during the process of reducing sulfates are very stable due to having the solubility significantly lower than metal oxides, metal hydroxides or metal carboates, there is no risk of re-elution. Most heavy metals can form the metal sulfides through the reaction with sulfates under the general anaerobic condition. In particular, even Mn, Zn and Al and so forth, which hardly precipitates as the forms of hydroxides or carboates, may react with the sulfides, to form a stable compound and to be stabilized.

The heavy metals may exist in the form of salts or simple substances in the landfills of trash or wastes. The heavy metals existing as the dissolved form in the landfills of trash 4or wastes may move as the ionic state, and such pathway for the heavy metal to be insolubilized may be called to comprise the steps of adsorption and precipitation. The adsorbed heavy metals can move again when the adsorption reaches the saturation point or the adsorbents are decomposed. Therefore, it may be mentioned that the final insolubilization of heavy metals in the landfill is mainly carried out by the precipitation.

The metal sulfides formed by binding sulfides and heavy metals may be the stable compounds in the solid form, unless being affected by the external condition such as aerobic environment or low pH value. The reason is that since the solubility of metal sulfides is extremely low, the heavy metal scarcely eluded from the metal sulfides. In the meantime, the landfills filled with the trash and/or wastes usually provide the anaerobic or almost anaerobic condition and pH ranging from 6 to 10. Therefore, once the metal sulfides formed, they are not re-eluded.

The solubility products of metal sulfides at 25°C are provided in Table 1 as shown below:

Table 1

Metal Sulfides	K_{sp}
Ag_2S	6.3×10^{-50}
CdS	8.0×10^{-27}
CoS	4.0×10^{-21}
CuS	6.0×10^{-36}
FeS	6.0×10^{-18}
HgS	1.6×10^{-52}
MnS	2.5×10^{-10}
NiS	3.0×10^{-19}
PbS	2.5×10^{-50}
SnS	1.0×10^{-25}
ZnS	1.1×10^{-21}

As seen from Table 1, it is found that most of all metal sulfides remain as the almost stable compounds in solid form, and the elution occurs only in extremely few cases.

Fig. 5 shows the insolubility of heavy metals caused by the sulfate-reducing bacteria. The initial concentrations of the heavy metal were set as follows: 20mg/l of Hg,

10mg/l of Cd, 10mg/l of Pb, 10mg/l of Ni, 5mg/l of Cu and 10mg/l of Mn.

According to the result of experiment, within a quarter of a day, more than 50% amounts of most heavy metal was removed by the sulfate-reducing bacteria, and in particular, in case of heavy metals such as Cu, Hg, Pb or Cd, 99% or more amounts of heavy metals were removed.

The result of experiment shows that the heavy metals contained in the incineration ash can be insolubilized by precipitating them as metal sulfides. As a result, it is expected that the possible contamination of soil and underground water due to the elution of heavy metal in the treatment of incineration ash can significantly be decreased.

The present invention uses the sulfate-reducing bacteria in order to solidify the harmful heavy metal contained in the incineration ash into the precipitates in the stable form of metal sulfides. In this regard, since like the most of organism, the sulfate-reducing bacteria also use the energy, which has been obtained during the anabolism such as the decomposition of organic compounds, a certain organic material should also be provided in order to utilize the metabolism of the sulfate-reducing bacteria. Since the sulfate-reducing bacteria use the various organic compounds as the carbon source, they are in the advantageous position relative to the other microorganisms in an aspect of competition for securing the organic compounds.

Since the sulfate-reducing bacteria is an anaerobic or at least almost anaerobic microorganism, an anaerobic or at least almost anaerobic condition should be provided for the sulfate-reducing bacteria to grow in the said environment. As a matter of fact, the sulfate-reducing bacteria may be distributed to a high density in an organic waste in which an anaerobic condition of ecological environment has been set up.

The representative examples of the organic waste in which the sulfate-reducing

bacteria exist include the sewage sludge, the drainage sludge, the dirty riverbed sludge and so forth (hereinafter, called as "sewage sludge").

The reason for the sulfate-reducing bacteria to exist in the sewage sludge to a high density is the anaerobic condition provided by the sewage sludge as well as the sufficient amount of organic compounds contained in the sewage sludge, which the sulfate-reducing bacteria decompose in order to obtain the energy.

Table 2 was provided to explain the latest fact, in which the result of analyzing elements sampled from the sewage sludge obtained from the various sewage disposal plants.

Table 2

Sludge sampled from	C(%)	H(%)	N(%)	S(%)
Nanji septic plant	42.838	6.118	4.176	0.944
Nanji sewage 1	18.082	3.131	2.622	1.295
Nanji sewage 2	19.376	3.177	3.055	1.172
Kayang sewage 1	18.532	3.797	3.052	1.172
Kayang sewage 2	20.177	3.797	3.052	1.430
Kayang septic plant	45.443	6.476	4.955	0.000
Jungryang sewage 1	27.491	4.223	3.320	1.588
Jungryang sewage 2	17.858	2.713	2.458	1.133
Tan-Stream A	20.729	3.578	3.231	1.258
Tan-Stream (mixed)	20.472	3.633	3.077	1.270

As seen from Table 2, when seeing the resulting data of analyzing elements sampled from the sewage sludge, it was found that relatively large amount of carbon element (17 to 45%) and nitrogen (2.5 to 5.0%) were contained in the sludge. Furthermore, although not provided to Table 2, the amount of contents as well as that of eluent of heavy metal is very low in the sewage sludge. Therefore, it may be found that

the sewage sludge has the condition for growing the sulfate-reducing bacteria.

Table 3 shows the compared density of the sulfate-reducing bacteria existing in sewage sludge from the various provinces in Korea.

Table 3

Sludge sampled from	(MPN/ml)
Nanji sewage 1	2.8×10^6
Nanji sewage 2	1.1×10^8
Nanji septic plant	1.1×10^8
Tan-Stream sewage	1.1×10^8
Tan-Stream septic plant	1.1×10^8
Kayang sewage 1	1.1×10^8
Kayang sewage 2	9.3×10^6
Kayang septic plant	4.6×10^7
Keumcheon the drainage	4.6×10^7
Jungryang sewage 1	1.5×10^7
Jungryang sewage 2	4.6×10^7
Incineration ash	0

As seen from Table 3, when seeing the resulting data of analyzing elements sampled from the sewage sludge, it was also found that relatively large amount of sulfate-reducing bacteria were contained in the sludge. However, no sulfate-reducing bacterium exists in the incineration ash.

An alternative example of the organic waste containing the sulfate-reducing bacteria includes the soil from the paddy field. The sulfate-reducing bacteria exist as mainly being a form of condensed accumulation sizing from several tens to hundreds of ㎛ in the soil of paddy field, and exist as a form of condensed accumulation in stream bed.

Furthermore, An alternative example of the organic waste containing the sulfate-

reducing bacteria includes the landfills of trash and/or wastes.

Table 4 provides the result of determining the density of sulfate-reducing bacteria existing in the trash and/or wastes filled in Nanji-do landfill.

Table 4

Depth of filling-up (m)	1 (MPN/ml)		2 (MPN/ml)	
	30° C	50° C	30° C	50° C
0-6	1.5×10^5	2.1×10^3	7.0×10^2	43
6-12	1.5×10^5	40	1.5×10^4	2.4×10^3
12-18	1.5×10^3	40	7.0×10^2	7.0×10^2
18-24	9.3×10^2	7.0×10^2	4.6×10^4	1.1×10^5
24-30	4.3×10^2	90	1.1×10^5	2.4×10^4
30-36	2.3×10^2	1.5×10^2	2.1×10^3	4.6×10^4
36-42	7.5×10^4	4.3×10^4	2.4×10^2	70
42-48	4.3×10^2	2.4×10^2	1.5×10^2	4.3×10^2
48-54	2.4×10^3	1.5×10^3	1.5×10^3	2.4×10^3
54-60	4.3×10^4	4.3×10^3	4.6×10^4	9.3×10^2

As shown in Table 4, not a little amount of sulfate-reducing bacteria was distributed in the trash/wastes buried in Nanji-do landfill, up to 10^5MPN/ml. Furthermore, although not shown in Table 4, not a little amount of sulfate-reducing bacteria was also distributed in the trash/wastes from the other landfills.

Aforementioned, the reason that not a little amount of sulfate-reducing bacteria exists in the sampled trash/wastes from the landfills is that the landfills of the trash/wastes adjust the anaerobic condition, and the various kinds of organic material exist in a mass.

According to another aspect of the present invention, a method is provided for removing the heavy metal in the incineration ash by using the sulfate-reducing bacteria existing in the natural system with the anaerobic condition of the ecological environment,

which includes the organic wastes. In other words, the present invention uses sulfur component contained in the incineration ash, and the organic material and the sulfate-reducing bacteria contained in the organic wastes, in order to treat the harmful heavy metal in the incineration ash in a stable manner.

The propagation of sulfate-reducing bacteria in the incineration ash and the reduction of sulfates may be explained by the following experiments.

Considering that the common landfills exhibit at least almost anaerobic or fully anaerobic condition with a low level of Oxidation-Reduction Potential (ORP), each 50 grams of bottom ash and fly ash and 500ml of distilled water were introduced into a 1000ml volume of container, and 4g of sewage sludge were added. After reducing by use of CO_2 gas and sealing, the bacteria in the container were cultured at 30° C. After 2 to 3 days, ORP value was determined as being –300mV or below, and the color was changed to red, which represents the propagation of sulfate-reducing bacteria.

Furthermore, it was reported that the addition of aqueous soil extract containing the sulfate-reducing bacteria to the incineration ash in a glass culumn tube promote the reduction of sulfates.

Therefore, since the sulfate-reducing bacteria can actively act in the common landfills exhibiting at least almost anaerobic or fully anaerobic condition with a low level of Oxidation-Reduction Potential (ORP), a co-treatment of the incineration ash and the sewage sludge fulfills the said condition.

As mentioned above, in a treatment of the incineration ash, the use of organic wastes as the sulfate-reducing bacteria may result in a synergic effect enabling the co-treatment of heavy metal as well as organic material in the organic wastes. Furthermore, it is possible to increase the ratio of removing the heavy metals in the incineration ash by

the anaerobic condition formed by the sulfate-reducing bacteria as well as the other kinds of bacteria existing in the organic wastes and decomposing the organic compounds. Furthermore, the organic wastes themselves can also be stabilized due to the active anabolism of sulfate-reducing bacteria.

In other words, in case that the incineration ash (sulfates + heavy metal) and the organic wastes (organic material + sulfate-reducing bacteria) containing the sulfate-reducing bacteria are co-treated, an effect of insolubilizing the heavy metal and removing the organic material may result, and it may be applied to the treatment of a hardly decomposing organic material or the wastewater containing the heavy metal and the wastewater sludge.

Brief Description of Drawings

Fig. 1 shows the amount of heavy metals contained in the incineration ash.

Fig. 2 shows the amount of heavy metals eluate exuding out of the incineration ash.

Fig. 3 shows the result of analysis for the elements of the incineration ash by use of element analyzer.

Fig. 4 shows the schematic pathway of the sulfates to be reduced into the sulfides by the sulfate-reducing bacteria.

Fig. 5 shows the insolubility of heavy metals caused by the sulfate-reducing bacteria.

Fig. 6 schematically shows the process of Example 1 for carrying out the method for treatment of the incineration ash according to the invention.

Figs. 7a to 7d provide the explanation of the types of the unit stacks buried in the landfill.

Figs 8a to 8c schematically show the process of Example 2 for carrying out the method for treatment of the incineration ash according to the invention.

Best Mode for Carrying Out the Invention

Hereinafter, a novel method according to the present invention will be described in detail by the examples for land-filling the incineration ash containing the heavy metal and the wastewater sludge, which comprises the first steps of removing the organic materials together with heavy metals, recovering the heavy metals, and using the conventional structure for utilizing the sulfate-reducing bacteria in the burying plant according to the reasonable plan in consideration of the properties of mutual relation between the bacteria and landfill.

Example 1 according to the method of the invention for treatment of the incineration ash provides a filling-up structure of landfill, which comprises: the first layer including the incineration ash and sewage sludge, and another layer covering the first layer with soil.

Fig.6 schematically shows the process of Example 1 for carrying out the method for treatment of the incineration ash according to the invention.

As shown in the drawings, below portion of the filling-up structure of landfill is provided a waterproofing barrier(61) and a drainage net system of leachate(62), and such units of the filling-up structure(63) are arranged to comprise the repeated layers. Each unit of the filling-up structure(63) should be covered by the layer of covering soil(64).

As seen from Figs. 7a to 7d, the units of the filling-up structure(63) may be constructed in the various manner of accumulating or mixing the incineration ash and sewage sludge.

For instance, as seen from Fig. 7a, after filling up the sewage sludge (A), the incineration ash (B) is filed up on the first layer, and the layer of covering soil (64) may be covered; as seen from Fig. 7b, after filling up the mixed trash (A+B) comprising the sewage sludge (A) and the incineration ash (B), the layer of covering soil (64) may be covered; as seen from Fig. 7c, after filling up the sewage sludge (A), the city trash (C) and the incineration ash (B) are sequentially filed up on the first layer, and the layer of covering soil (64) may be covered; or as seen from Fig. 7d, after filling up the mixed trash (A+B+C) comprising the sewage sludge (A), the incineration ash (B) and the city trash (C), the layer of covering soil (64) may be covered.

The filling-up structure of landfill having the predetermined size may be formed by the repeated work for constructing the units of filling-up structure (63). On the upper end of the filling-up structure in landfill, the final layer of covering soil (66) is laid. The reference number 67, which was not explained, indicates a bank supporting such filling-up structure of landfill, and the reference number 67 indicates the drainage for flowing out the rainwater.

In the filling-up structure of landfill, the other portions of the plant except those for filling-up may follow the general standard required for filling-up industry.

As aforementioned, in a unit of the filling-up structure (63), the sulfate-reducing bacteria in the sewage sludge convert the sulfate (SO_4^{-2}) into the sulfides (S^{-2}) using the energy produced during the anabolism of the bacteria which utilize the organic material in the sewage sludge, and the sulfides (S^{-2}) binds to the heavy metal in the incineration ash to form a insoluble metal sulfides in a solid form. Therefore, the heavy metal in the incineration ash is solidified to stable metal sulfides in the units of the filling-up structure (63). Since the components in the landfill are hardly eluded in the leachate and so forth,

the heavy metals in the incineration ash can be stabilized in an insoluble form.

The remaining leachate from the sewage sludge or the city trash after the step of filling up, may be drained through the drainage net system of leachate(62). The leachate drained through the drainage net system of leachate(62) may flow out through another route, such as leachate pool or reaction chamber, or re-injected into the landfill to carry out the leachate recycling pathway, by which the effects of insolubilization and stabilization of the heavy metals in the incineration ash may be amplified by the adopted bacteria.

Figs 8a to 8c schematically show the process of Example 2 for carrying out the method for treatment of the incineration ash according to the invention.

Example 2 provides a method for treatment of leachate from the landfills in which the incineration ash, the city trash and the sewage sludge have been separately filled up, by treating them with the anaerobic condition.

Referring to Fig. 8a, the leachate (81) from the region of the incineration ash and the leachate (82) from the region of the sewage sludge in the landfill are collected in one reaction plant (85). To this, the leachate (83) from the region of the city trash may also be added for using the sulfate-reducing bacteria from the region of the city trash.

The reference number 86, which was not explained, indicates the mixture of each leachate from the incineration ash, the sewage sludge and the city trash.

Referring to Fig. 8b, in the mixture (86) in the reaction plant (85), the heavy metals existing in the leachate from the incineration ash may be precipitated by the action of sulfate-reducing bacteria in the sewage sludge. The mechanism of such reaction was aforementioned.

Referring to Fig. 8c, the precipitated heavy metal (87) and the remaining reaction

product (88) are separately drained out and treated. In this stage, since the precipitated heavy metal (87) may be recovered through the additional apparatus for recovering the heavy metal, an advantage of the possible re-use of resources may be accomplished. Furthermore, since the reaction production may contain an amount of the sulfate-reducing bacteria adopted to the anaerobic condition, it may be reused in the process for treatment of the incineration ash.

Industrial Applicability

The present invention enables the conversion of heavy metals in the incineration ash into the stable metal sulfides in the form of insolubilized precipitates, thereby significantly reducing the possibility of contaminating the surrounding soils and underground water caused by the elution of heavy metals during the treatment of incineration ash. Furthermore, in case that an organic waste such as the sewage sludge which contains the sulfate-reducing bacteria as the sulfate-reducing microorganism source, a synergic effects for treating the heavy metals existing in the sludge may also be expected. Moreover, another kinds of bacteria existing in the waste sludge besides the sulfate-reducing bacteria may amplify the effect for removing the heavy metals from the incineration ash. Such active metabolism of the sulfate-reducing bacteria can effectively promote the stabilization of sewage sludge.

The invention can solve the problems related to the treatment and disposal of the large amount of waste sludge and incineration ash, by the method according to the invention for treating the incineration ash containing the heavy metal and the wastewater sludge, which makes the heavy metal existing in the incineration ash insoluble and results in the stabilization of organic material by burying them in the conventional structure for

burying plant according to the reasonable plan in consideration of the properties of mutual relation between them.

Furthermore, although it was difficult for securing a region suitable for using as the landfills and much cost were consumed under the circumstance of the prior arts, it is the advantage of the invention that it may not be difficult any more for securing the region for using as the landfills, and not much costs are required for the process, due to filling up the incineration ash together with city trash.

Although the present invention have specifically been described by way of the detailed examples, it is not intended to limit the spirit and scope of the invention within those description, and the skilled man in the art will be able to embody the various changes without departing from the scope of the invention as described in the specification and claimed in the attached claims.

WHAT IS CLAIMED IS:

1. A method of treating the incineration ash and the wastewater sludge, wherein a mutual relation in using nutrients exists between the incineration ash containing the heavy metal and the organic wastes containing the wastewater sludge and sulfate-reducing bacteria, comprising the steps of:

burying the incineration ash together with the organic wastes under the ground, in which the bacteria reduce the sulfates existing in the incineration ash to form the sulfides;

binding the formed sulfides with the heavy metal to form the insoluble metal sulfides, in order to prevent the heavy metal from exuding out of the incineration ash as the eluate.

2. The method for treatment of the incineration ash and the wastewater sludge as claimed in claim 1, characterized in that the said organic wastes comprise the sewage sludge containing the said sulfate-reducing bacteria.

3. A method for treatment of the incineration ash and the wastewater sludge, comprising: burying the incineration ash together with the organic wastes containing the sulfate-reducing bacteria under the ground, and covering them with a depth of soil, so that the said sulfate-reducing bacteria promote the heavy metal to precipitate in the form of dissoluble metal sulfides, in order to prevent the heavy metal from exuding out of the incineration ash as the eluate.

4. The method for treatment of the incineration ash and the wastewater sludge as claimed in claim 3, characterized in that two or more unit stages of the buried

accumulation, each of which includes the incineration ash and the organic wastes containing the sulfate-reducing bacteria, are constructed in a predetermined pattern of arrangement, and the layer of covering soil forms a barrier which defines the boundary between the said unit stages of the buried accumulation.

5. The method for treatment of the incineration ash and the wastewater sludge as claimed in claims 3 or 4, characterized in that the said organic wastes comprise the sewage sludge containing the said sulfate-reducing bacteria.

6. A method for treatment of the incineration ash and the wastewater sludge, which comprising the steps:

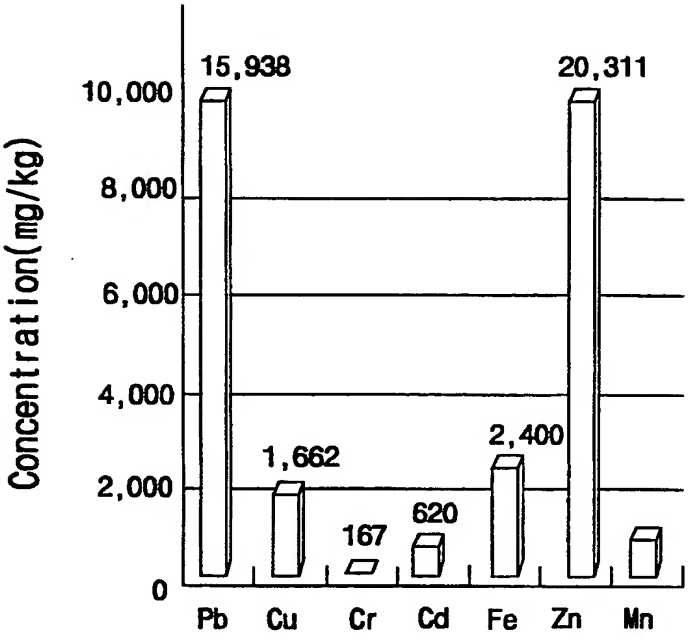
collecting and mixing the aqueous eluate exuding out of the incineration ash and the aqueous eluate exuding out of the organic waste containing the said sulfate-reducing bacteria in a disposal plant; and

reacting both the aqueous elutes so that the said sulfate-reducing bacteria existing in the aqueous eluate exuding out of the organic waste deposits the heavy metals from the aqueous eluate exuding out of the incineration ash as the insoluble metal sulfides, which results in the disposal of the aqueous eluate exuding out of the incineration ash and the aqueous eluate exuding out of the organic waste.

7. The method for treatment of the incineration ash and the waste as claimed in claim 6, characterized in that a portion of the precipitated insoluble metal sulfides is extracted from the reaction plant, and only the desired heavy metal is recovered through the further reaction process, in order to reuse the resources.

8. The method for treatment of the incineration ash and the waste as claimed in claim 6, characterized in that the said organic wastes comprise the sewage sludge containing the said sulfate-reducing bacteria.

FIG.1


Concentration(mg/kg)
10,000
8,000
6,000
4,000
2,000
0
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1,662
167
620
2,400
20,311
Pb
Cu
Cr
Cd
Fe
Zn
Mn

FIG.2

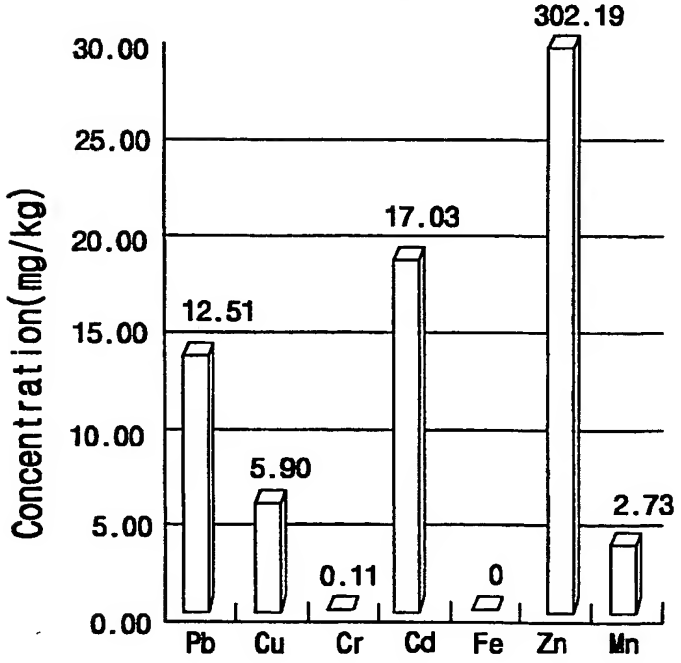

Concentration(mg/kg)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
12.51
5.90
0.11
17.03
0
302.19
2.73
Pb
Cu
Cr
Cd
Fe
Zn
Mn

FIG.3

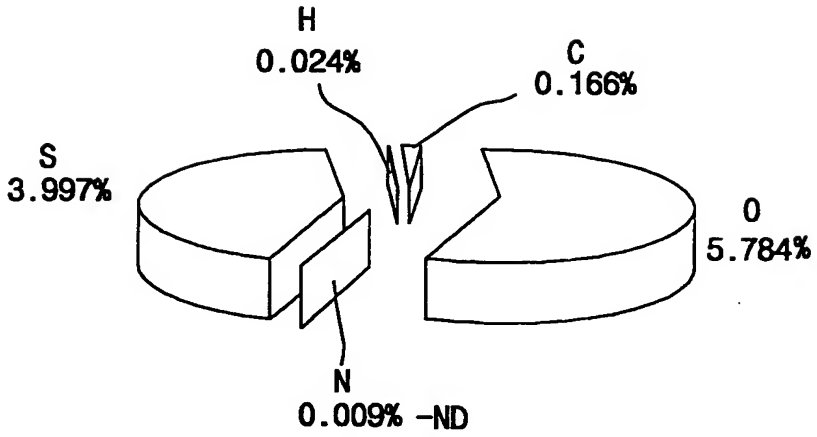
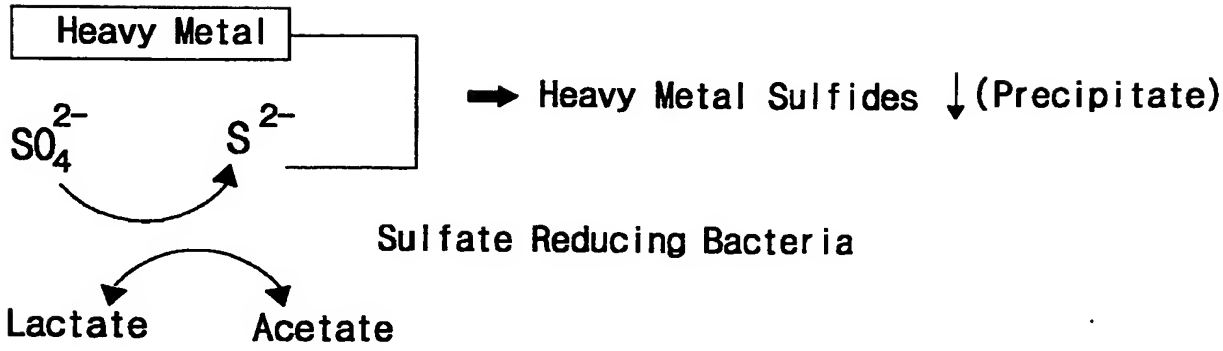


FIG.4



$$2CH_3CH(OH)COO^- + H_2SO_4 \longrightarrow 2CH_3COO^- + 2CO_2 + H_2S + 2H_2O$$

$$SO_4^{2-} + 2(CH_2O) + 2H^+ \longrightarrow H_2S + 2CO_2 + 2H_2O$$

FIG.5

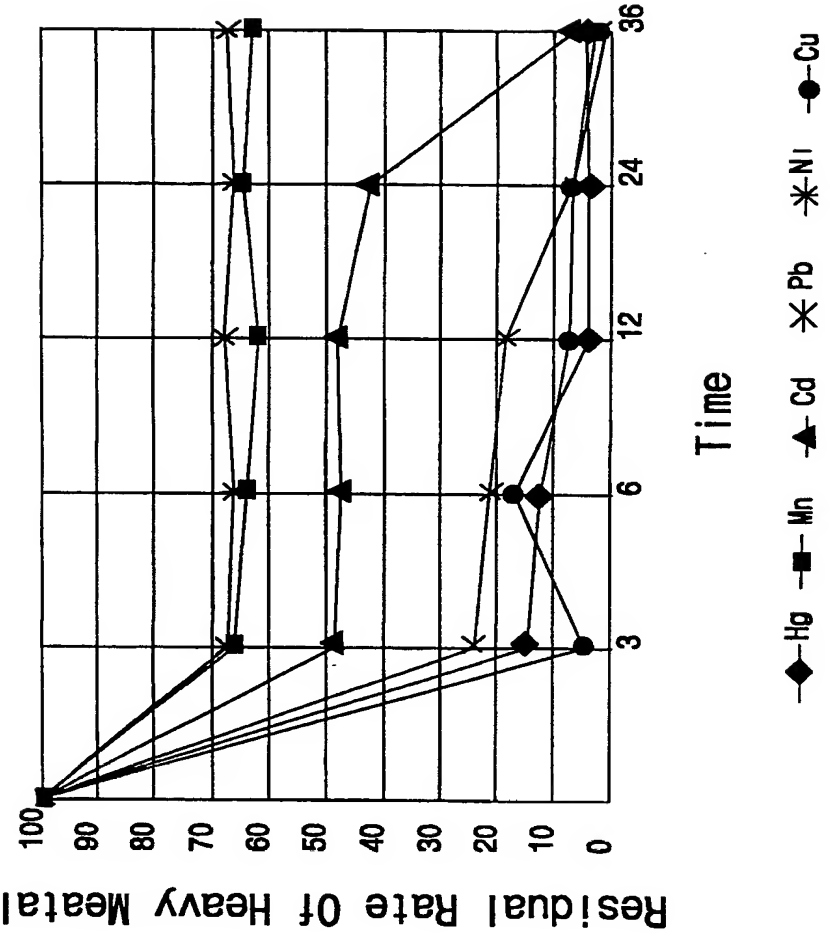

Residual Rate Of Heavy Metals (%)
100
90
80
70
60
50
40
30
20
10
0
3
6
12
24
36
Time
Hg
Mn
Cd
Pb
Ni
Cu

FIG.6

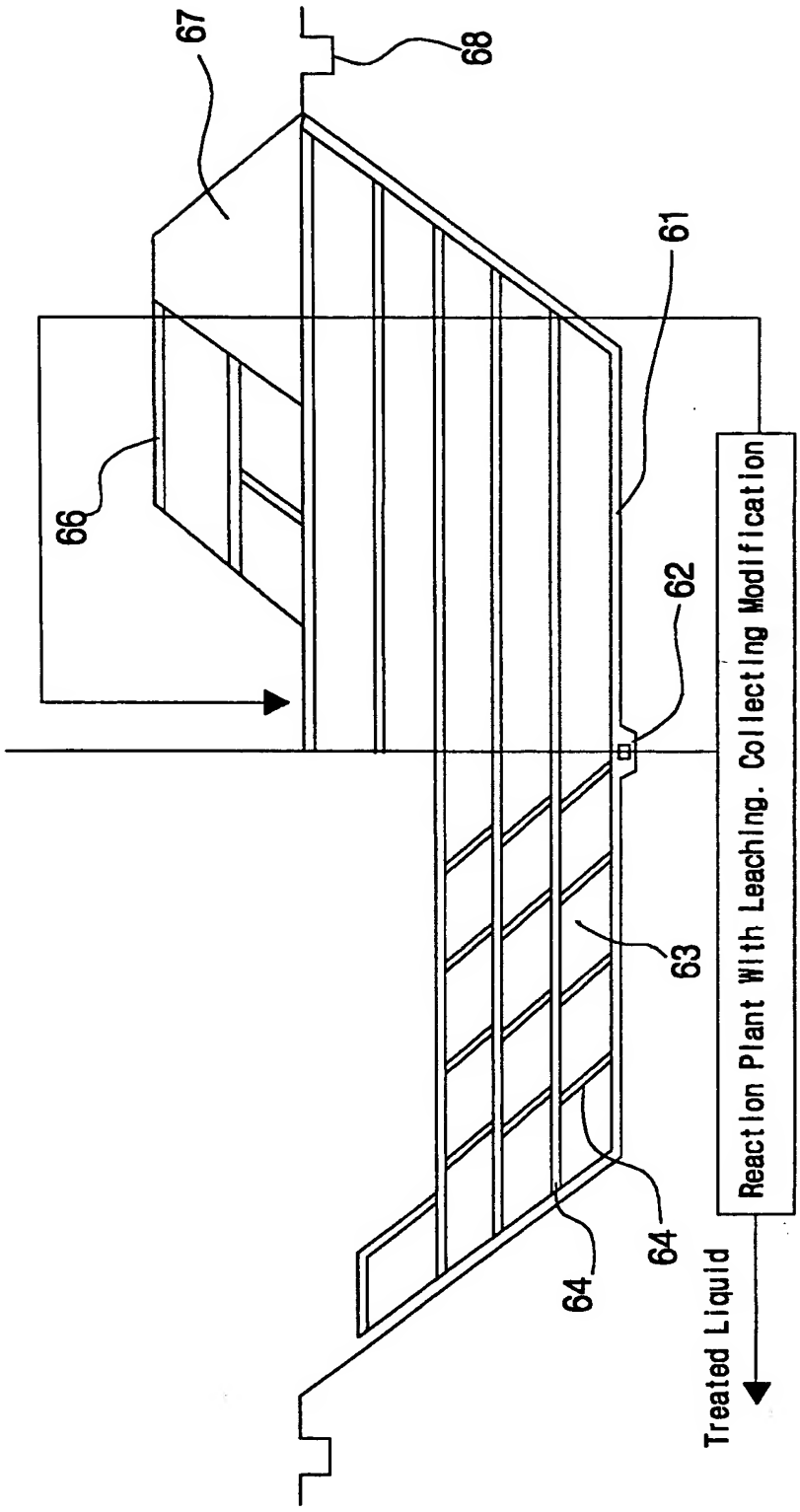

67
68
61
66
62
63
64
64
Reaction Plant With Leaching. Collecting Modification
Treated Liquid

FIG.7A

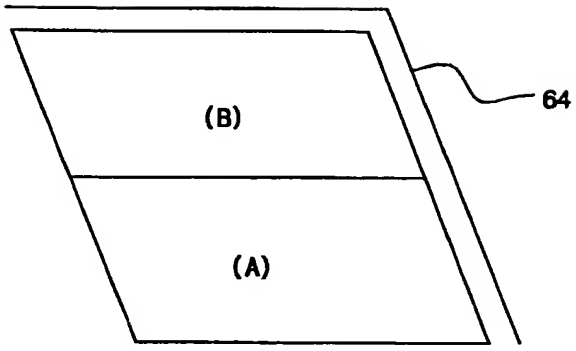


FIG.7B

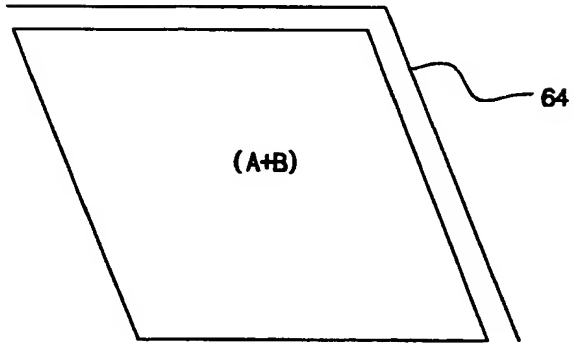


FIG.7C

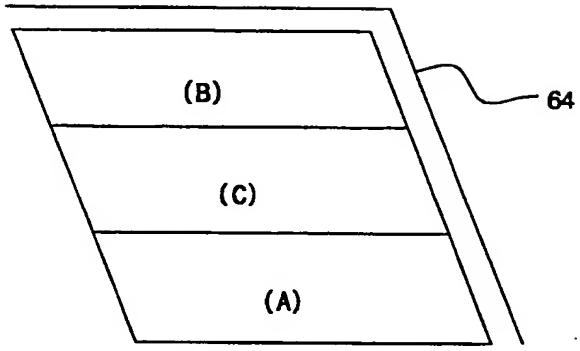


FIG.7D

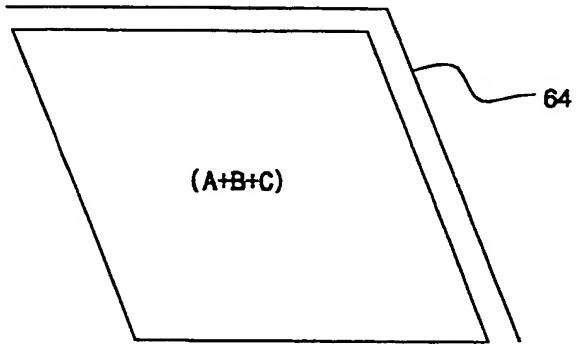


FIG.8A

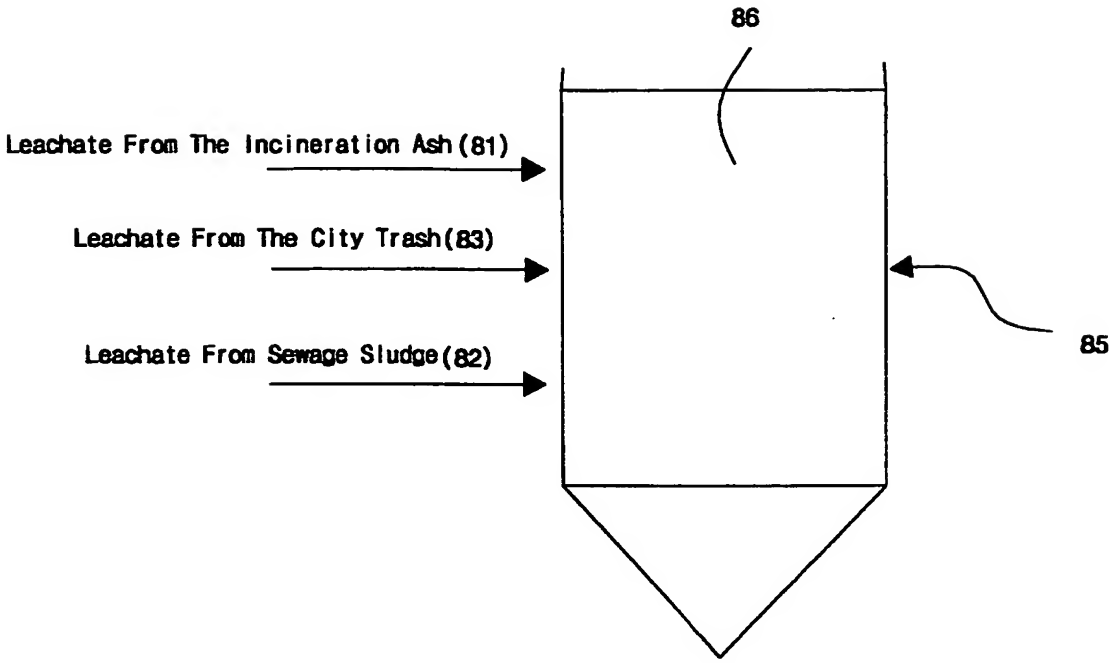

86
Leachate From The Incineration Ash(81)
Leachate From The City Trash(83)
Leachate From Sewage Sludge(82)
85

FIG.8B

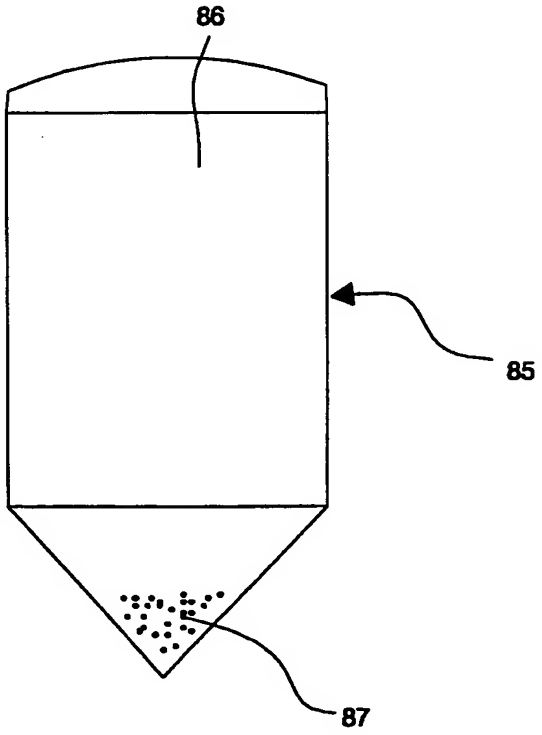
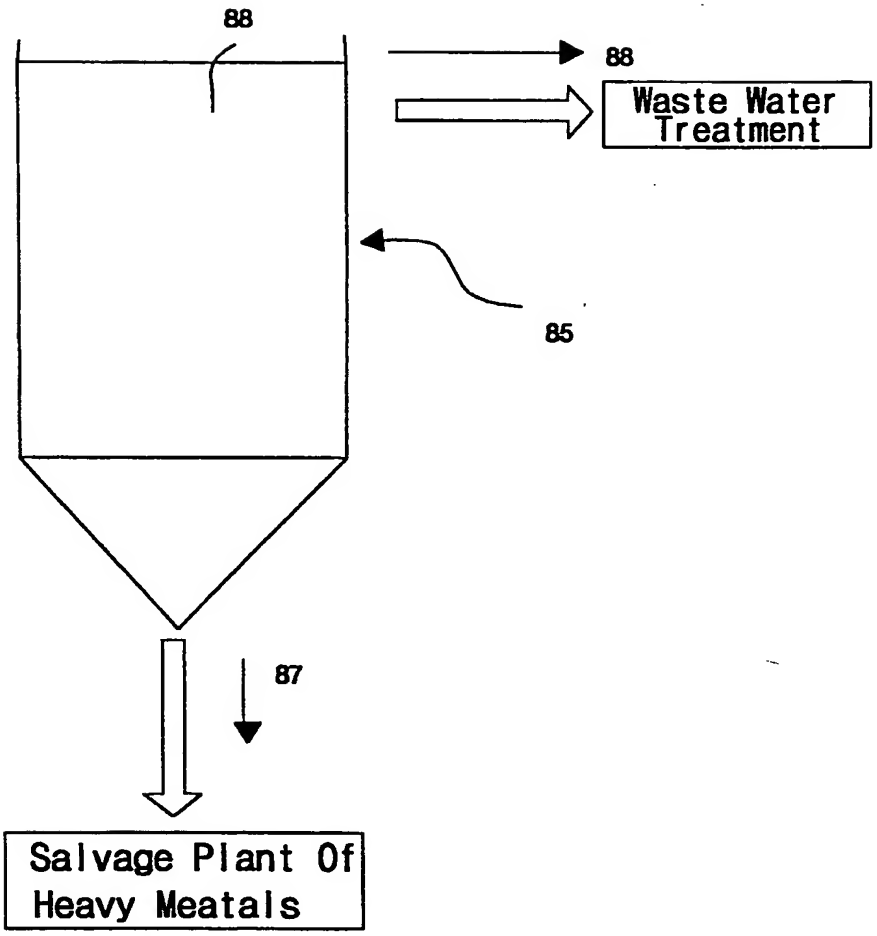

86
85
87

FIG.8C


88
88
Waste Water Treatment
85
87
Salvage Plant Of Heavy Meatals

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/00922

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C02F 11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)
IPC7 C02F A62D 3/00

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched
Korean Patents and applications for inventions since 1975
Korean Utility models and applications for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search trerms used)
NPS, IPN, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95/022375 A1 (ECCLES, Harry) 24 August 1995 see the whole document,	1- 8
A	KR 1998-67148 A (Korea Institute of Science and Technology) 15 October 1998 see the whole document,	1- 8
A	US 4,354,937 A (Vyrmetoder AB) 19 October 1982 see the whole document,	1- 8
A	US 4,522,723 A (Kerr-McGee Corporation) 11 June 1985 see the whole document,	1- 8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevence
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevence; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevence; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 DECEMBER 2000 (08.12.2000)	09 DECEMBER 2000 (09.12.2000)

Name and mailing address of the ISA/KR	Authorized officer
Korean Industrial Property Office Government Complex-Taejon, Dunsan-dong, So-ku, Taejon Metropolitan City 302-701, Republic of Korea	WON, Jong Hyeok
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-5592

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR00/00922

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 95/022375 A1	24. 08. 95	RU2133632C1	27.07.99
		JP9522375 W1	24.08.95
		EP744982 A1	04.12.96
		US5840191 A	11.24.98
KR 1998-67148 A	15.10.98	None	
US 4,354,937 A	19.10.82	None	
US 4,522,723 A	11.06.85	None	

RECORD COPY

PCT REQUEST

00PCT-09JK

Original (for **SUBMISSION**) - printed on 18.08.2000 03:54:19 PM

0 **0-1**	**For receiving Office use only** International Application No.	PCT/KR 00/00922
0-2	International Filing Date	18 August 2000 (18.08.00)
0-3	Name of receiving Office and "PCT International Application"	Korean Industrial Property Office PCT International Application
0-4 0-4-1	**Form - PCT/RO/101 PCT Request** Prepared using	PCT-EASY Version 2.91 (updated 01.07.2000)
0-5	**Petition** The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	**Receiving Office (specified by the applicant)**	Korean Industrial Property Office (RO/KR)
0-7	**Applicant's or agent's file reference**	00PCT-09JK
I	**Title of invention**	METHOD OF TREATING INCINERATION ASHES WITH SULFATE REDUCING BACTERIA
II	**Applicant**	
II-1	This person is:	applicant and inventor
II-2	Applicant for	all designated States
II-4	Name (LAST, First)	JUNG, Kweon
II-5	Address:	#1316-1601, Tongbaek Apt., Sanbon-dong 435-040 Kunpo-shi, Kyonggi-do Republic of Korea
II-6	State of nationality	KR
II-7	State of residence	KR
II-8	Telephone No.	82-2-570-3381
II-9	Facsimile No.	82-2-570-3475
III-1	**Applicant and/or inventor**	
III-1-1	This person is:	applicant only
III-1-2	Applicant for	all designated States except US
III-1-4	Name (LAST, First)	SHIN, Jai-Young
III-1-5	Address:	#Ra-1205, Sora Apt., Pangbae-dong, Seocho-ku 137-060 Seoul Republic of Korea
III-1-6	State of nationality	KR
III-1-7	State of residence	KR

PCT REQUEST 00PCT-09JK

Original (for **SUBMISSION**) - printed on 18.08.2000 03:54:19 PM

III-2	**Applicant and/or inventor**	
III-2-1	This person is:	applicant only
III-2-2	Applicant for	all designated States except US
III-2-4	Name (LAST, First)	KIM, Min-Young
III-2-5	Address:	288-1 Kyohyon-ri, Changheung-myon 482-810 Yangju-kun, Kyonggi-do Republic of Korea
III-2-6	State of nationality	KR
III-2-7	State of residence	KR
IV-1	**Agent or common representative; or address for correspondence** The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	YANG, Soon-Seok
IV-1-2	Address:	Durey Patent Office #401, Kangnam-Jeil Bldg., 822-4 Yoksam-dong, Kangnam-ku 135-080 Seoul Republic of Korea
IV-1-3	Telephone No.	82-2-569-4653
IV-1-4	Facsimile No.	82-2-569-4655
IV-1-5	e-mail	yangpat@chollian.net
V	**Designation of States**	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	JP US
V-5	**Precautionary Designation Statement** In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	**Exclusion(s) from precautionary designations**	NONE

PCT REQUEST 00PCT-09JK

Original (for **SUBMISSION**) - printed on 18.08.2000 03:54:19 PM

VI-1	**Priority claim of earlier national application**		
VI-1-1	Filing date	19 August 1999 (19.08.1999)	
VI-1-2	Number	[99]-34333 (1999)	CORRECTED BY RO
VI-1-3	Country	KR	
VII-1	**International Searching Authority Chosen**	Korean Industrial Property Office (KIPO) (ISA/KR)	
VIII	**Check list**	number of sheets	electronic file(s) attached
VIII-1	Request	3	-
VIII-2	Description	17	-
VIII-3	Claims	2	-
VIII-4	Abstract	1	00pct-09jk.txt
VIII-5	Drawings	8	-
VIII-7	TOTAL	31	
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-9	Separate signed power of attorney	✓	-
VIII-12	Priority document(s)	Item(s) VI-1	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-18	**Figure of the drawings which should accompany the abstract**	6	
VIII-19	**Language of filing of the international application**	Korean	
IX-1	**Signature of applicant or agent**		
IX-1-1	Name (LAST, First)	YANG, Soon-Seok	

FOR RECEIVING OFFICE USE ONLY

10-1	**Date of actual receipt of the purported international application**	18 August 2000 (18.08.00)
10-2	**Drawings:**	
10-2-1	Received	
10-2-2	Not received	
10-3	**Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application**	
10-4	**Date of timely receipt of the required corrections under PCT Article 11(2)**	
10-5	**International Searching Authority**	ISA/KR
10-6	**Transmittal of search copy delayed until search fee is paid**	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	**Date of receipt of the record copy by the International Bureau**	13 SEPTEMBER 2000	(13.09.00)

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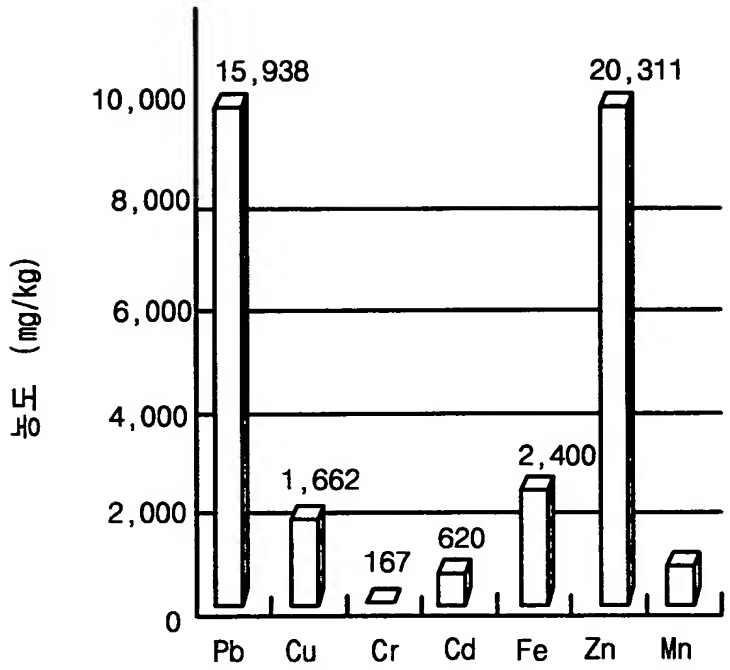
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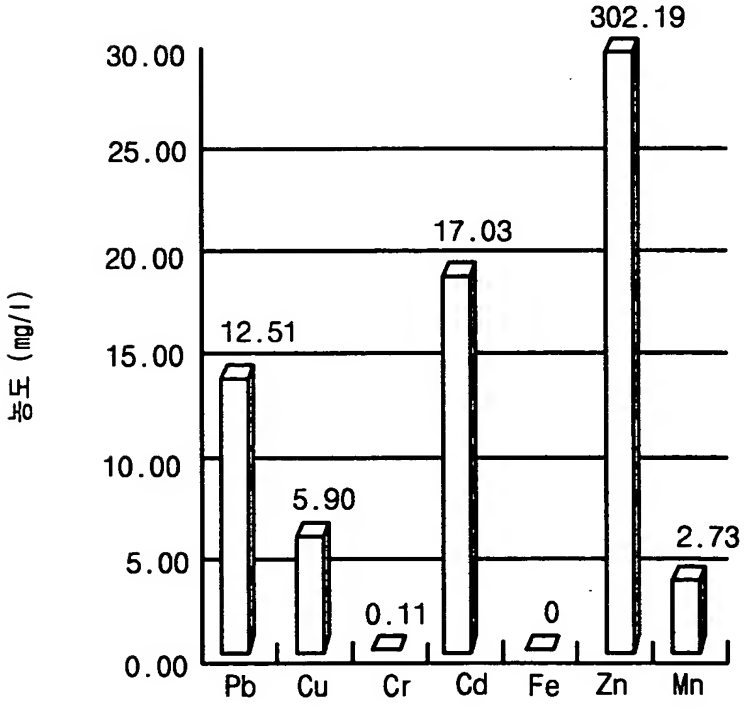
Cd
Fe
Zn
Mn

도 2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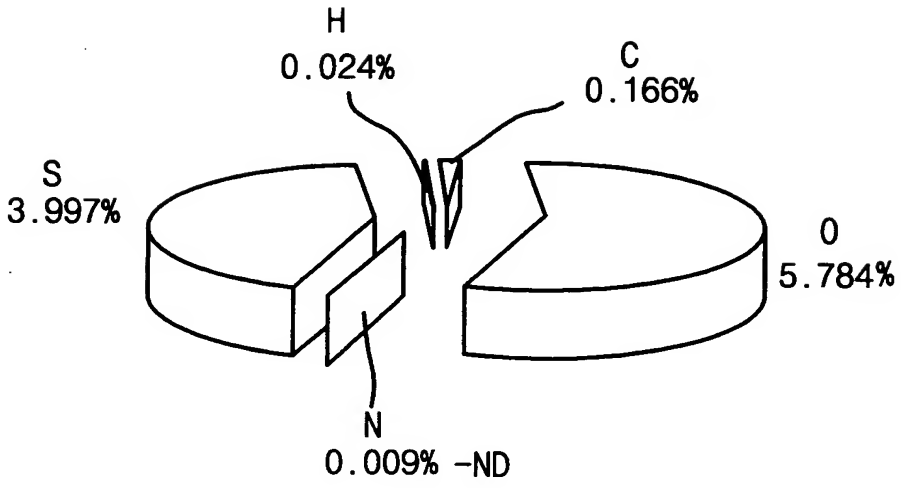
도 3



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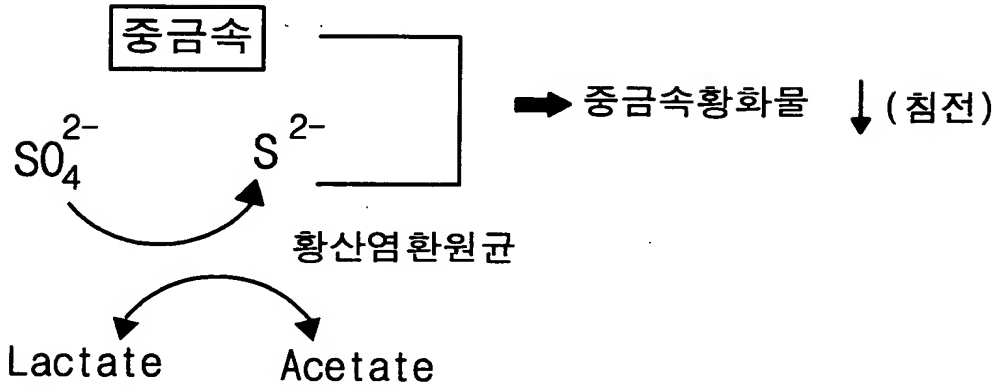
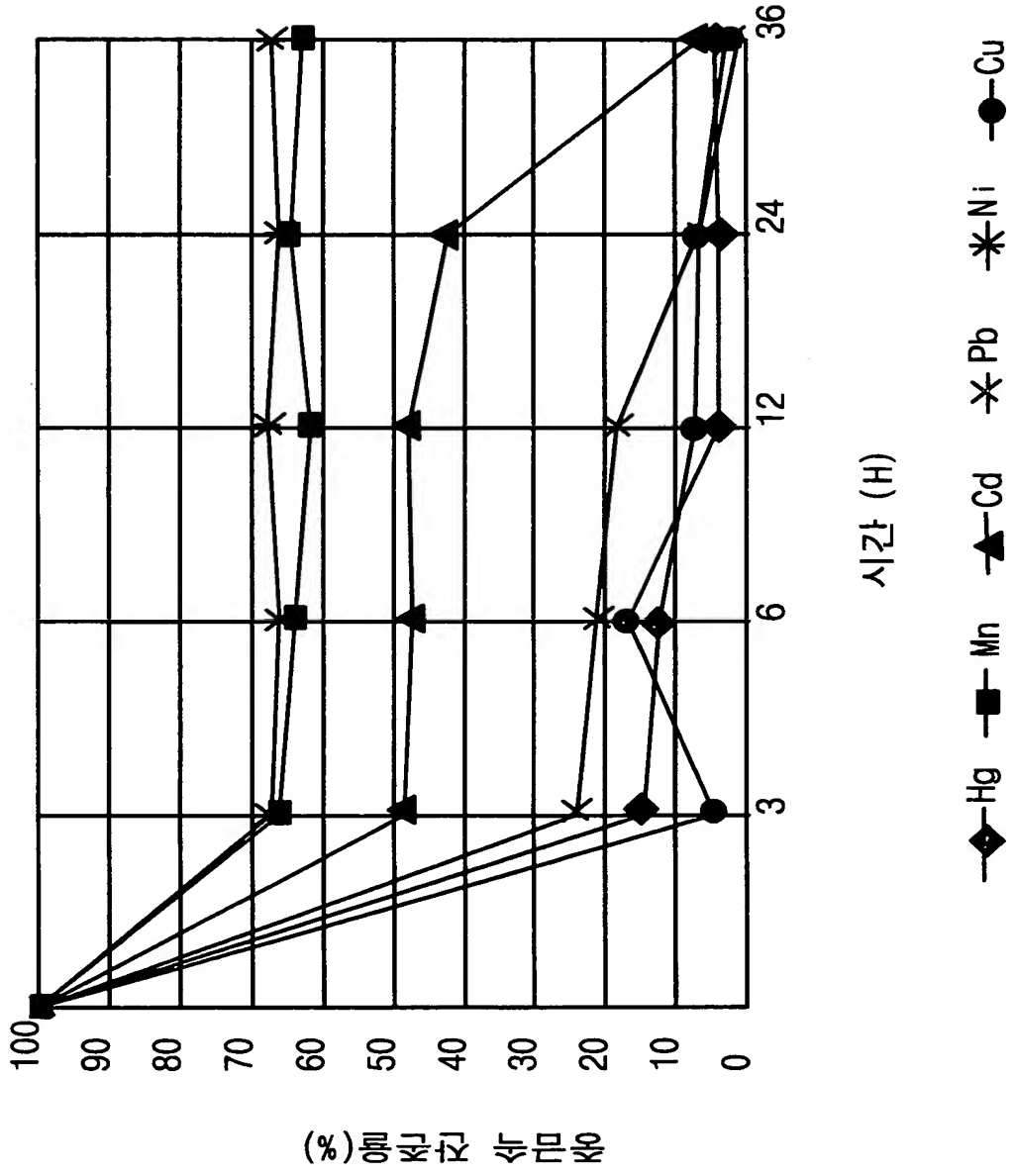
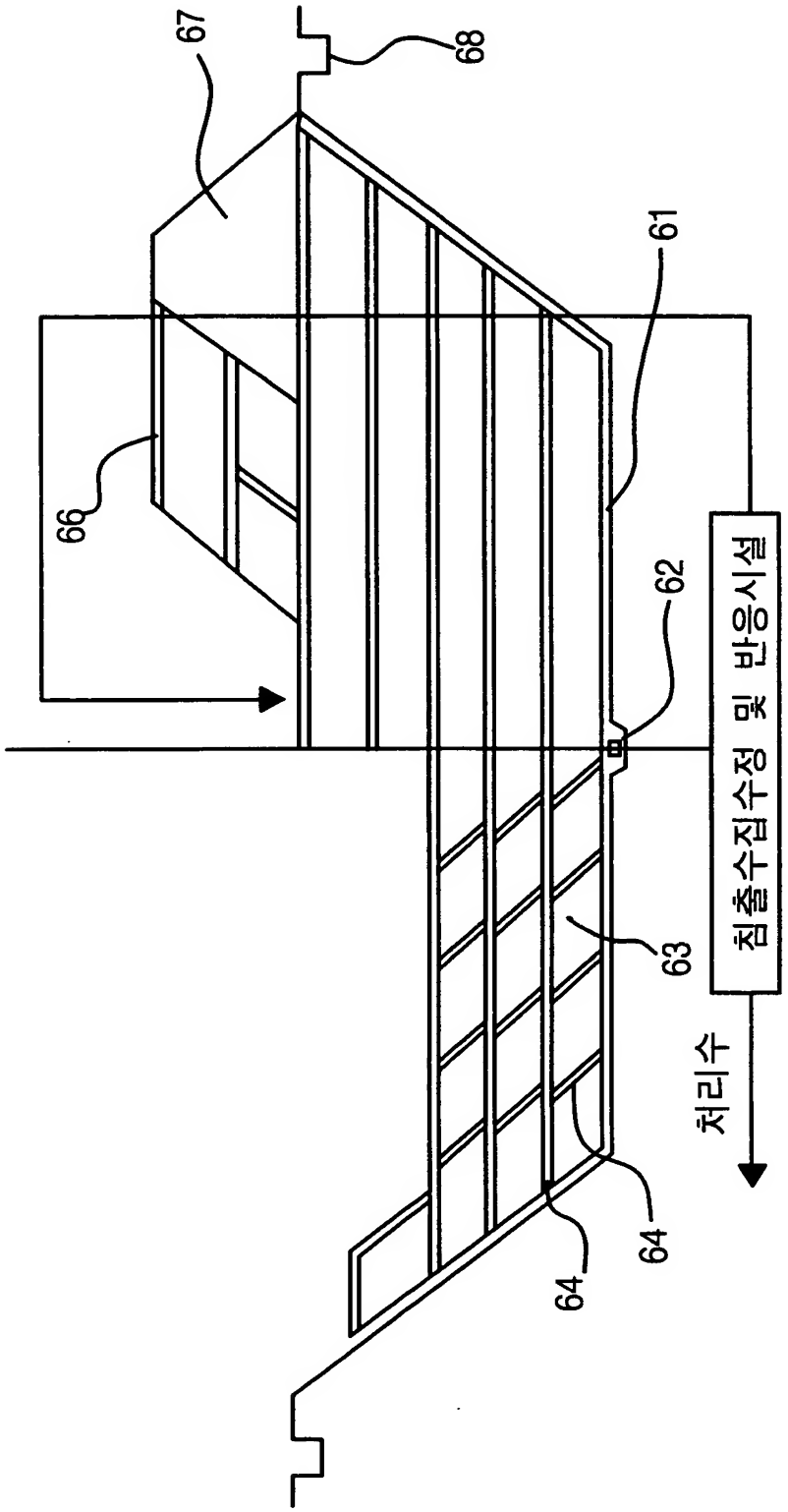


$$2CH_3CH(OH)COO^- + H_2SO_4 \longrightarrow 2CH_3COO^- + 2CO_2 + H_2S + 2H_2O$$

$$SO_4^{2-} + 2(CH_2O) + 2H^+ \longrightarrow H_2S + 2CO_2 + 2H_2O$$

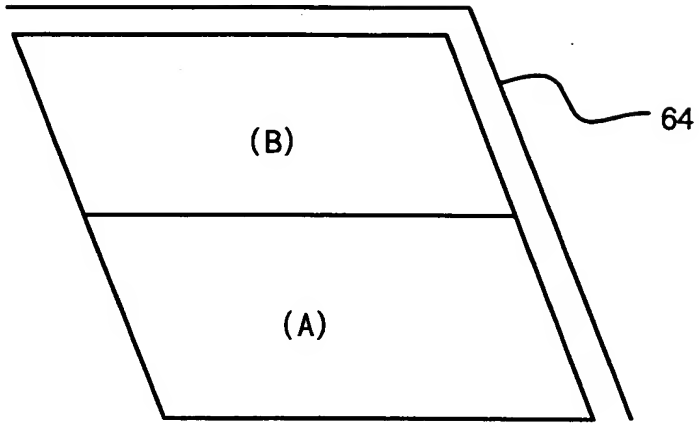
도 5





도 6

도 7A



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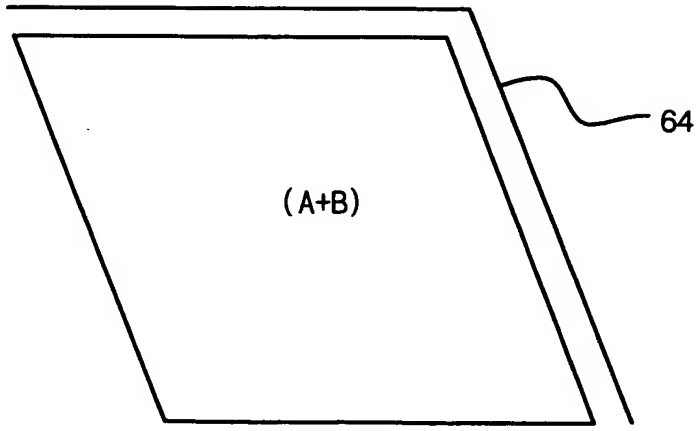
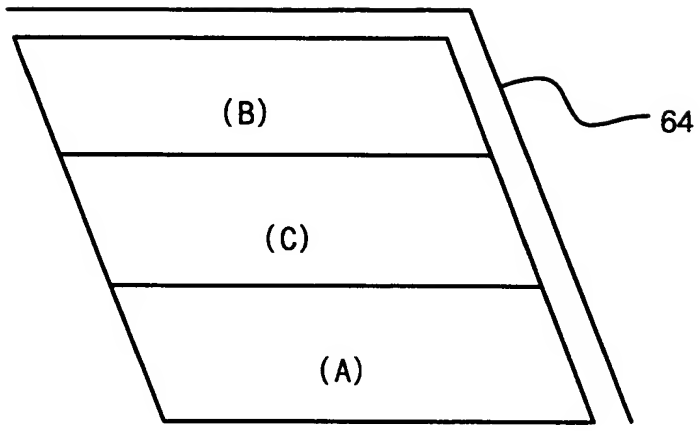


도 7C



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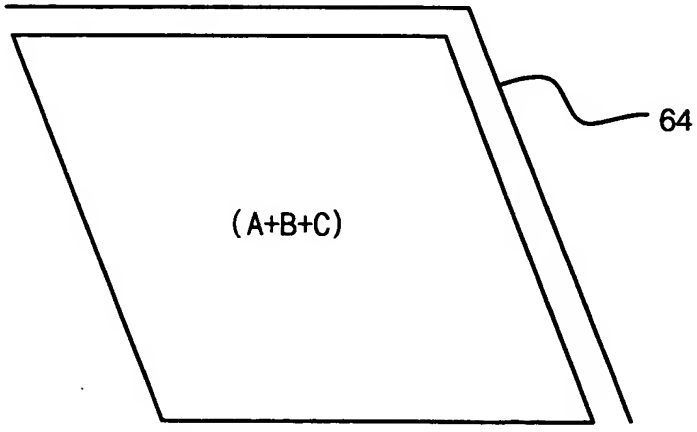

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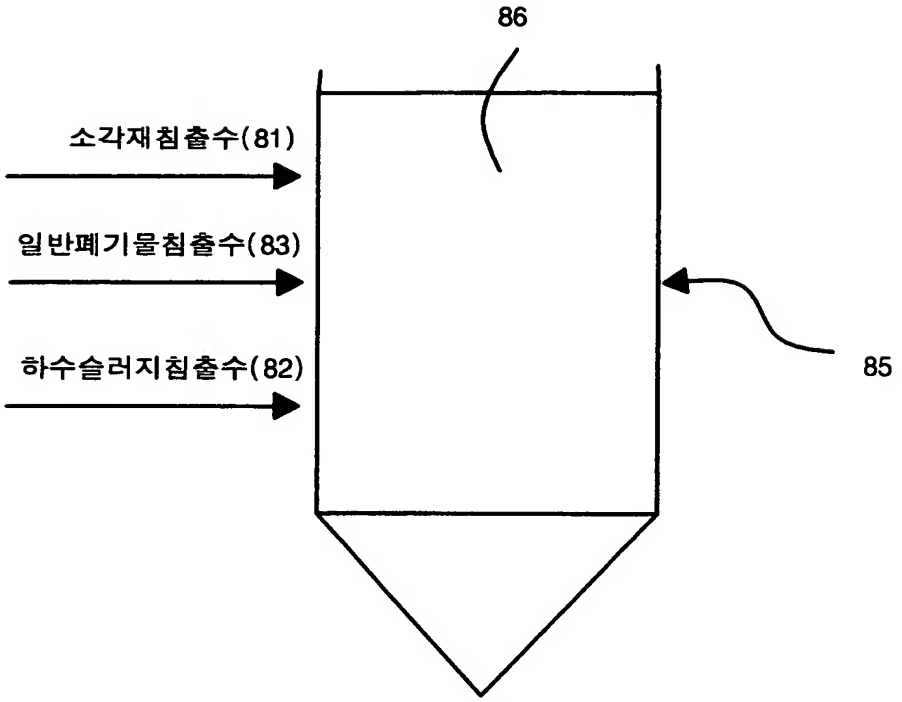

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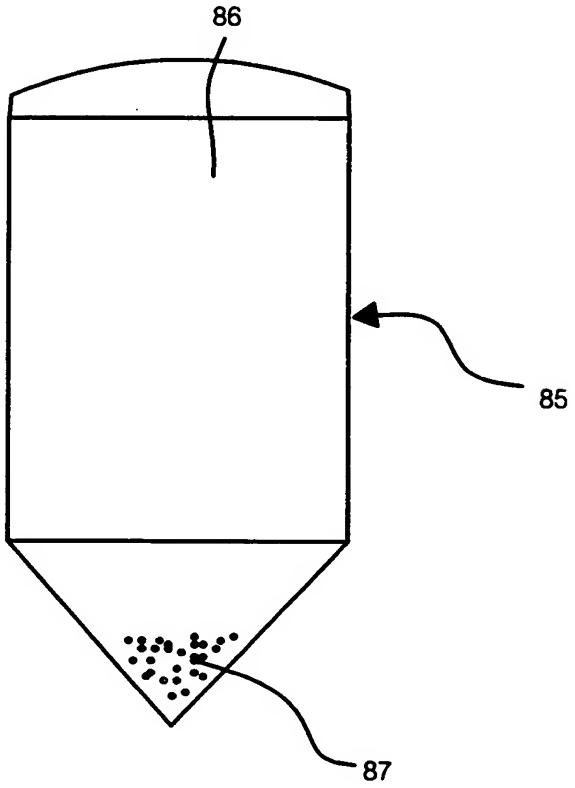

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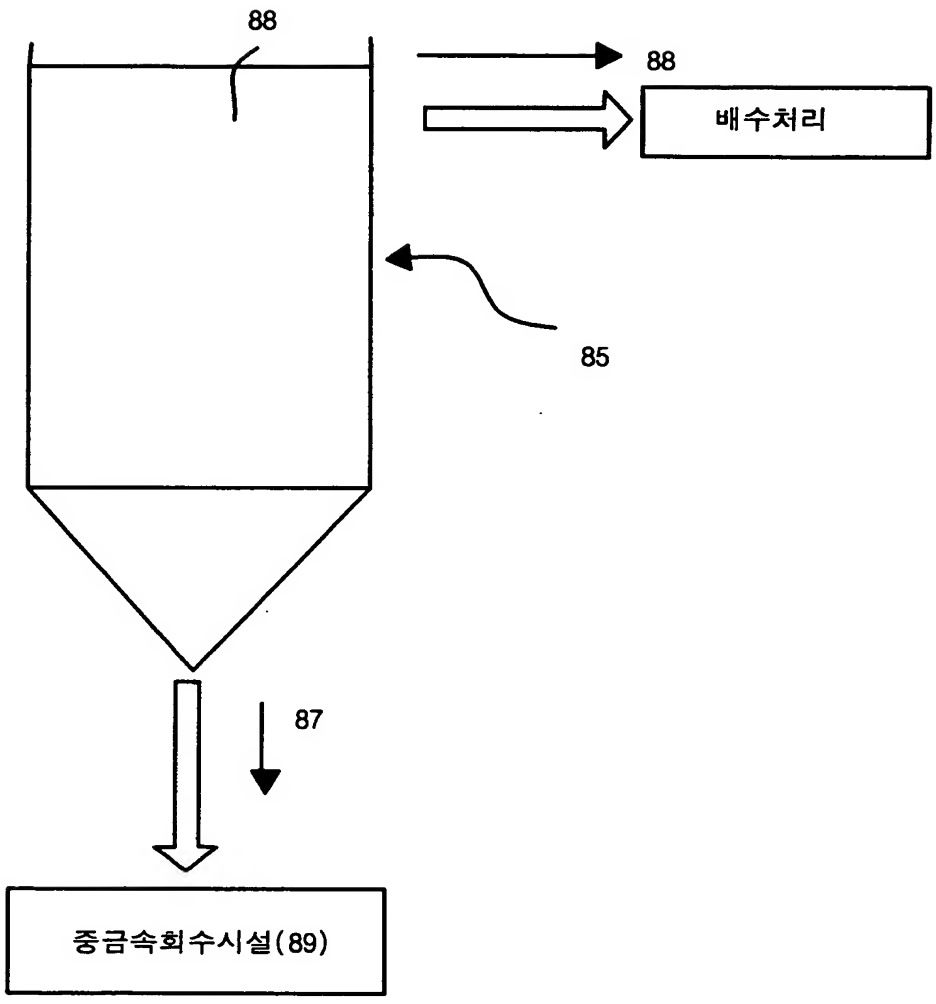

명 세 서

황산염환원균을 이용한 소각재 및 폐수슬러지 처리방법

기술분야

본 발명은 중금속을 함유하는 소각재(incineration ash) 및 폐수슬러지 처리방법에 관한 것으로 특히, 황산염환원균 (Sulfate Reducing Bacteria)을 이용하기 위하여, 기존의 매립시설 구조에 매립물의 상호보완적 특성을 고려하여 합리적이며 계획적으로 매립하여 소각재의 중금속을 불용화시키고 유기물의 안정화를 유도하는 중금속을 함유하는 소각재 및 폐수슬러지 처리방법에 관한 것이다.

배경기술

최근 새로운 도시문제중의 하나로 대두되고 있는 고형 폐기물을 처분하는 방법은 주로 매립처리 방법에 의존하고 있다. 그러나 우리나라와 같이 국토 면적이 좁은 나라에서는 넓은 면적을 필요로 하는 매립장의 부지확보가 어려우며, 매립지 수명연장 차원에서 소각처리 방법이 그 대안으로 추진되고 있다.

폐기물을 소각처리하고 그 잔재만을 매립처분하는 경우 매립폐기물의 부피를 85~90% 줄일 수 있기 때문에 매립장의 사용년한을 높일 수 있는 장점이 있다.

소각재를 처리하기 위하여, 고형화제와 소각재를 혼합기에 넣고 물을 주입하여 혼합시킨 후 고형화시키는 통상적 고형화법과 소각재에 화학약품을 첨가하여 소각재 내의 중금속을 화학적으로 안정화시키는 화학적 고형안정화법 등이 제시되고 있다.

그러나, 통상적 고형화법은 소각재의 감용효과가 적고 시멘트중의 중금속이 pH에 따라 용출될 수 있으므로 중금속의 용출될 가능성이 크며 처리비용도 높다는 단점이 있다. 또한, 화학적 고형안정화법은 고가의 화학약품(킬레이트제)을 사용해야하고, 그에 따라 또 다른 오염원을 발생시키는 단점이 있으며, 여전히 pH에 따라 중금속의 용출가능성이 크다는 단점이 있다.

도 1과 도 2는 이를 설명하기 위한 도면들로, 노원소각 시설에서 나온 소각재에서의 중금속 함유량과 중금속 용출량을 각각 나타낸 것이다. 도 2는 TCLP법에 의하여 용출시험된 결과를 나타낸 것이다.

중금속 전함유량을 보여주는 도 1에 보인 바와 같이, 소각재 중 중금속은 Pb가 15,936 ㎎/㎏, Cd가 620 ㎎/㎏, Cu가 1,662 ㎎/㎏, Zn이 20,311 ㎎/㎏ 등으로 다량으로 함유하고 있다.

또한, 소각재의 원소 분석의 결과로 질소(N)는 거의 없고 황(S)성분이 3.997%까지 함유되어 있다.

중금속 용출량을 보여주는 도 2에 보인 바와 같이, 소각재 중 중금속은 Zn이 302.19 ㎎/ℓ, Pb이 12.51 ㎎/ℓ, Cd가 17.03 ㎎/ℓ, Cu가 5.90 ㎎/ℓ으로 다량의 중금속이 용출되어 현재 기준을 상당히 초과하고 있다.

이와 같이, 각종 소각 대상 폐기물 중에 존재하는 미량 중금속은 소각과정에서 제거되지 않고 필연적으로 소각잔재(바닥재 및 비산재) 중에 농축된 후, 집진시설에서 포집되어 남게 되며, 그 농도는 소각전 폐기물 중의 농도보다 고농도로 농축되어 존재하게 된다. 이들 바닥재와 비산재 중에 함유되어 있는 중금속은 매립처분시에 우수(雨水)에 용출되어 침출수화되며, 지하수 오염 및 토양 오염 등의 2차 오염을 유발시킬 가능성이 크기 때문에 이에 대한 적절한

관리가 요구되고 있다.

발명의 상세한 설명

본 발명은 종래 기술에 따른 문제점을 해결하는 소각재 처리방법을 제공하고자 한다.

본 발명은 황산염환원균을 이용하여 중금속을 함유하는 소각재 및 폐수 슬러지 (이하, 소각재로 약칭함) 내의 중금속을 안전하게 불용화시켜서 소각재 내에 존재하는 중금속의 외부 용출을 방지하는 소각재 처리방법을 제공하고자 한다.

본 발명은 중금속을 불용화시키는 황산염환원균을 이용하여 소각재를 처리하되, 황산염환원균을 포함하는 유기성 폐기물에서 황산염환원균을 공급받을 수 있도록, 소각재와 유기성 폐기물을 함께 매립하는 소각재 처리방법을 제공하고자 한다.

이를 위한 본 발명은 소각재와 황산염환원균을 포함하는 유기성 폐기물과의 상호보완적 특성을 이용하여 상기 소각재와 상기 유기성 폐기물을 함께 매립하여, 상기 황산염 환원균으로 상기 소각재 내에 존재하는 황산염을 환원시켜 황화물을 생성시켜 상기 생성된 황화물을상기 소각재 내에 존재하는 중금속과 결합시켜 불용성 금속황화물을 형성하여 상기 소각재로부터 중금속이 외부로 용출되지 않도록 하는 소각재 처리방법을 제공한다.

또한, 본 발명은 소각재 내의 중금속을 황산염환원균이 불용성 금속황화물로 침전시켜 상기 소각재로부터 중금속이 외부로 용출되지 않도록 소각재 및 황산염환원균을 포함하는 유기성 폐기물을 함께 매립하고 복토를 덮어 매립물을 형

성하는 소각재 처리방법을 제공한다.

또한, 본 발명은 소각재를 매립한 지역에서 나오는 침출수와 황산염환원균을 포함하는 유기성 폐기물에서 나오는 침출수를 하나의 반응시설에 혼합하고 반응시켜, 상기 소각재 침출수 내에 용존하는 중금속을 상기 유기성 폐기물 침출수 내에 존재하는 황산염환원균이 불용성 금속황화물로 침전시켜 소각재의 침출수와 유기성 폐기물의 침출수를 처리하도록 구성되는 소각재 처리방법을 제공한다.

상기에서 황산염환원균을 포함하는 유기성 폐기물을 하수슬러지로 하여 본 발명을 구성할 수 있다.

이하, 첨부된 도면을 참조하여 본 발명을 설명하면 다음과 같다.

본 발명은 황산염환원균의 이화작용에 의하여 소각재 내에 존재하는 다량의 황산염(sulfate)을 황화물(sulfide)로 환원시켜 소각재 내의 중금속과 결합시킴으로써, 불용화된 금속황화물로 침전 및 제거하는 방법을 제공한다.

도 3은 원소분석기를 통하여 소각재의 원소를 분석한 것을 도면으로 나타낸 것이다. 소각재는 도면에 보인 바와 같이, 3.997%라는 다량의 황 원소가 존재한다.

황 원소는 소각재 내에서 산소와 결합하고, 소각재를 함유하는 용액에서는 황산염(SO_4^{2-})으로 존재한다.

황산염환원균을 이용하여 소각재 내의 황과 중금속이 결합하는 기구는 도 4를 참조하여 아래에서 설명한다. 도 4는 황산염환원균에 의하여 황산염(SO_4^{2-})이 황화물(S^{2-})로 환원하는 환원경로를 보여준다.

소각재 내의 황산염(SO_4^{2-})은 황산염환원균에 의하여 황화물(S^{2-})로 환원되고, 이 황화물은 소각재 내의 중금속과 결합하여 불용성의

금속황화물이라는 침전물을 만든다.

일반적으로 황산염환원균은 혐기성 세균으로, 유기물인 젖산(lactate acid)을 이용하여 에너지를 얻는데, 그 결과로 아세트산(acetate acid)등의 대사산물을 배출한다. 이와 같이, 황산염환원균은 유기화합물을 분해하는 이화과정을 통하여 황산염을 환원시킨다.

또한, 황산염환원균은 팔미틴산등 지방산이나 안식향산, 페놀등의 방향족 화합물 등을 분해할 수 있다.

생태계의 다양한 종류의 황산염환원균은 황산염(SO_4^{2-}) 같이 안정한 염을 분해하기 위하여는 높은 에너지가 필요하며, 메탄균과 함께 유기물의 최종분해자로 역할을 하고 있다.

즉, 황산염환원균은 생물학적 혐기성 환경 조건하에서 전자수용체로 작용하는 무기성 산화물인 황산염(SO_4^{2-})을 황화물(S^{2-}, HS^- 혹은, H_2S)로 환원시킨다. 이 때, 전자공여체로 이용되는 유기화합물이 산화된다. 이 때, 생성된 황화물(S^{2-}, HS^- 혹은, H_2S)과 소각재 내의 중금속은 친화력이 있어 결합하여 침전하게 된다.

이와 같은 황산염 환원 반응 과정에서 형성된 금속황화물은 금속산화물, 금속수산화물, 금속탄산화물보다 용해도가 훨씬 낮아서 매우 안정하므로 재용출의 염려가 없다. 대부분의 중금속은 일반적인 혐기 조건에서 황산염과 반응하여 금속황화물을 형성한다. 특히, 수산화물, 탄산화물 형태로는 잘 침전되지 않는 Mn, Zn, Al등도 황화물과 반응하여 안전한 화합물을 형성하여 불용화된다.

폐기물 매립지에서 중금속 형태는 염 또는 금속단체로 존재한다. 폐기물 매립지 내에서 용해되어 있는 중금속은 이온상태로 이동하는데 이런 이온 상태의 중금속 불용화 과정은 흡착과 침전이라고 할 수 있다. 흡착은 흡착량이 포화에

달하거나 흡착제 자체가 분해되면 다시 이동될 수 있다. 그러므로 매립지에서 최종 중금속 불용화는 침전에 의한 불용화가 주된 것이라 할 수 있다.

황화물과 중금속이 결합되어 이루어진 금속황화물은 외부에 영향 즉, 호기성 조건이나 낮은 pH 조건이 형성되지 않는 한 안정한 고체 화합물이다. 그 이유는 금속황화물의 용해도가 극히 낮아서 용출되는 경우가 극히 적기 때문이다. 한편, 폐기물 매립지는 준혐기성 내지 혐기성 조건이며, pH의 범위는 6~10 사이다. 그러므로, 일단 형성된 금속황화물은 재용출의 우려가 없다.

표 1은 25℃에서의 금속황화물의 용해도적을 보여준다.

【표 1】

금속황화물	Ksp
Ag_2S	6.3×10^{-50}
CdS	8.0×10^{-27}
CoS	4.0×10^{-21}
CuS	6.0×10^{-36}
FeS	6.0×10^{-18}
HgS	1.6×10^{-52}
MnS	2.5×10^{-10}
NiS	3.0×10^{-19}
PbS	2.5×10^{-50}
SnS	1.0×10^{-25}
ZnS	1.1×10^{-21}

표 1을 통하여 대부분의 금속황화물은 실온에서 거의 안전한 고체 화합물의 상태로 존재하며, 극히 낮은 용해도적을 가지는 특성으로 인하여 용출되는 경우가 극히 적음을 알 수 있다.

도 5는 황산염환원균에 의한 중금속 불용화를 설명하기 위한 도면이다.

중금속의 초기 농도는 Hg 20 mg / ℓ, Cd 10 mg / ℓ, Pb 10 mg / ℓ, Ni 10 mg / ℓ, Cu 5 mg / ℓ, Mn 10 mg / ℓ 로 설정한 것이다.

실험결과에 의하면, 대부분의 중금속은 반나절 정도가 지나면, 황산염환원균에 의하여 50%이상 제거된다. 특히, Cu, Hg, Pb, Cd와 같은 중금속의 경우에는 36시간이 지나면 99% 이상 제거됨을 알 수 있다.

이와 같은 실험결과는 황산염환원균에 의하여 소각재 내의 중금속을 안전한 금속황화물로 침전시켜 불용화시킬 수 있으며, 그 결과로 소각재를 처리함에 있어서 중금속의 용출로 인한 주변의 토양 및 수질 오염의 가능성을 획기적으로 줄일 수 있다는 것을 보여준다.

본 발명은 소각재 내에 존재하는 유해한 중금속을 안정적인 금속황화물이라는 침전물로 고형화시키기 위해서 황산염환원균을 이용한다. 그런데, 황산염환원균은 통상의 생물체와 같이, 유기화합물이 분해되어 가는 이화과정에서 얻은 에너지를 사용하기 때문에 황산염환원균의 대사작용을 이용하기 위해서는 유기물도 함께 공급되어야 한다. 황산염환원균은 다양한 유기물을 탄소원으로 이용하므로써 다른 미생물과 비교하여 유기물 확보경쟁에서 비교적 유리한 입장에 있다.

황산염환원균은 혐기성 혹은 준혐기성 미생물이므로, 황산염환원균이 자랄 수 있는 혐기성 혹은 준혐기성 조건을 갖추어 주어야 한다. 혐기적 생태환경

조건이 갖추어진 황산염환원균이 존재할 수 있는 유기성 폐기물에서는 황산염환원균이 고밀도로 분포되어 있다.

"황산염환원균이 존재하는 유기성 폐기물"의 대표적인 예로 하수슬러지, 하수관거슬러지 및 하상저질슬러지 등(이하, 하수슬러지라 통칭함)을 들 수 있다.

하수슬러지에 황산염환원균이 고밀도로 분포될 수 있는 것은 하수슬러지가 혐기성 조건을 갖추고 있을 뿐만 아니라, 황산염환원균이 에너지를 얻기 위하여 분해해야 하는 유기물을 다량 함유하고 있기 때문이다.

표 2는 이를 설명하기 위한 것으로, 여러 하수처리장에서 나온 하수슬러지를 원소분석한 결과를 나타낸 것이다.

【표 2】

구분	C(%)	H(%)	N(%)	S(%)
난지정화슬러지	42.838	6.118	4.176	0.944
난지하수슬러지1	18.082	3.131	2.622	1.295
난지하수슬러지2	19.376	3.177	3.055	1.172
가양하수슬러지1	18.532	3.797	3.052	1.172
가양하수슬러지2	20.177	3.797	3.052	1.430
가양정화슬러지	45.443	6.476	4.955	0.000
중랑하수슬러지1	27.491	4.223	3.320	1.588
중랑하수슬러지2	17.858	2.713	2.458	1.133
탄천A슬러지	20.729	3.578	3.231	1.258
탄천혼합슬러지	20.472	3.633	3.077	1.270

표 2에 보인 바와 같이, 하수 슬러지의 원소 분석 결과를 보면, 탄소(C)가

17~45%, 질소(N)가 2.5~5.0%로 상당량 함유되어 있음을 알 수 있다. 또한, 표에 보이지 않았지만, 하수슬러지에는 중금속 함유량이 매우 낮고, 중금속 용출량도 매우 낮다. 따라서, 하수슬러지에는 황산염환원균이 존재할 수 있는 조건을 갖추고 있음을 알 수 있다.

표 3은 국내 여러 지역의 하수 슬러지(sludge)에 존재하는 황산염환원균의 농도를 비교하여 나타낸 것이다.

【표 3】

구분	측정결과(MPN/mℓ)
난지 하수 슬러지(1)	2.8×10^{6}
난지 하수 슬러지(2)	1.1×10^{8}
난지 정화 슬러지	1.1×10^{8}
탄진 하수 슬러지	1.1×10^{8}
탄진 정화 슬러지	1.1×10^{8}
가양 하수 슬러지(1)	1.1×10^{8}
가양 하수 슬러지(2)	9.3×10^{6}
가양 정화 슬러지	4.6×10^{7}
금천 하수 관거 슬러지	4.6×10^{7}
중랑 하수 슬러지(1)	1.5×10^{7}
중랑 하수 슬러지(2)	4.6×10^{7}
소각재	0

여러 도시 하수처리장의 슬러지에서도 다량의 황산염환원균이 존재함을 알 수 있다. 10^{6}-10^{8} MPN/mℓ정도의 다량의 황산염환원균이 분포되어 있다. 그러나, 소각재 속에는 황산염환원균이 전혀 존재하지 않는다.

"황산염환원균이 존재하는 유기성 폐기물"의 다른 예로는 논토양을 들 수 있다. 논토양에서 황산염환원균의 존재 형태는 수십 ㎛ 내지 수백 ㎛의 크기로 주로 응집체형태로 존재하고, 하천저질 등에서도 응집체 형태로 존재한다.

또한, "황산염환원균이 존재하는 유기성 폐기물"의 또 다른 예로는 폐기물 매립지를 들 수 있다.

표 4는 난지도 매립지의 매립 폐기물에 존재하는 황산염환원균의 농도를 매립깊이별로 측정하여 나타낸 것이다.

【표 4】

매립깊이(m)	측정 1 (MPN/mℓ)		측정 2 (MPN/mℓ)	
	30℃	50℃	30℃	50℃
0-6	1.5×10^5	2.1×10^3	7.0×10^2	43
6-12	1.5×10^5	40	1.5×10^4	2.4×10^3
12-18	1.5×10^3	40	7.0×10^2	7.0×10^2
18-24	9.3×10^2	7.0×10^2	4.6×10^4	1.1×10^5
24-30	4.3×10^2	90	1.1×10^5	2.4×10^4
30-36	2.3×10^2	1.5×10^2	2.1×10^3	4.6×10^4
36-42	7.5×10^4	4.3×10^4	2.4×10^2	70
42-48	4.3×10^2	2.4×10^2	1.5×10^2	4.3×10^2
48-54	2.4×10^3	1.5×10^3	1.5×10^3	2.4×10^3
54-60	4.3×10^4	4.3×10^3	4.6×10^4	9.3×10^2

난지도 매립지의 매립 폐기물에도 최대 10^5MPN/mℓ정도의 적지 않은 황산염

환원균이 분포되어 있고, 표에 나타내지 않았지만, 타매립지에서도 황산염환원균이 상당량 분포되어 있다.

이와 같이, 조사된 폐기물 매립지에 황산염환원균이 적지 않게 존재하는 이유는, 폐기물 매립지는 혐기성 조건을 갖추고 있을 뿐만 아니라, 각종 유기물이 다량 존재하기 때문이다.

본 발명은 소각재 처리방법의 다른 실시예로 황산염환원균 원(源)으로 별도로 제조된 배양물을 사용하지 않고서도, 혐기적 생태환경 조건이 갖추어진 자연계 즉, 황산염환원균을 포함하는 유기성 폐기물에 존재하는 황산염환원균을 이용하여 소각재의 중금속을 제거하는 경우를 제시한다. 즉, 소각재의 유해한 중금속을 안정적으로 처리하기 위하여 소각재에 함유되어 있는 황 성분과 유기성 폐기물에 존재하는 유기물 및 황산염환원균을 사용한다.

소각재 중 황산염환원균의 증식 및 황산염환원은 다음 설명되는 실험에 의하여 확인된다.

매립장이 보통 낮은 레벨의 ORP(산화환원전위)의 준혐기성 내지 혐기성을 나타내는 것을 감안하여, 1000㎖의 용기에 바닥재 및 비산재에 대하여 각각 50g과 증류수 500㎖를 가하고 하수슬러지 4g을 넣고 CO_2가스로 중화시키고 밀폐 후, 30℃에서 배양하였다. 그 결과, 2-3일 후 ORP는 -300㎷이하로 되고 흑변하여 황산염환원균의 증식을 확인할 수 있었다.

또한, 소각재를 넣은 유리칼럼관에 황산염환원균이 존재하는 토양식종액을 가하면 황산염환원이 진행한다고 보고되고 있다.

따라서, 낮은 레벨의 ORP(산화환원전위)의 준혐기성 내지 혐기성을 나타내고 있는 매립장에서는 황산염환원균이 활발히 활동할 수 있으므로,

소각재와 하수슬러지의 상호보완적 공동처분은 이러한 조건을 충분히 만족시킬 수 있다.

상술한 바와 같이, 소각재를 처리하는 데 있어서, 황산염환원균원으로 유기성 폐기물을 사용할 경우에는 유기성 폐기물의 유기물 및 중금속도 함께 처리할 수 있는 상승효과도 기대할 수 있다. 또한, 황산염환원균 뿐만 아니라 유기성 폐기물 에 존재하는 다른 종류의 유기물 분해균에 의한 혐기성 조건에 의하여 소각재 내의 중금속 제거율을 상승시킬 수 있다. 또한, 황산염환원균의 활발한 이화작용으로 인하여 유기성 폐기물의 안정화도 함께 도모할 수 있다.

즉, 소각재(황산염+중금속)에 황산염환원균을 포함하는 유기성 폐기물(유기물 + 황산염환원균)을 공동처리할 경우 상호 보완적 작용에 의하여 중금속 불용화 및 유기물질 제거에 효과가 있으며, 향후에 난분해성 유기물질이나 중금속함유 폐수 및 폐수 슬러지 등의 처리에 적용 가능하다.

도면의 간단한 설명

도 1은 소각재에서의 중금속 함유량을 나타낸 도면

도 2는 소각재에서의 중금속 용출량을 나타낸 도면

도 3은 원소분석기를 통하여 소각재의 원소를 분석한 도면

도 4는 황산염환원균에 의하여 황산염이 황화물로 환원하는 환원경로를 보여주는 도면

도 5는 황산염환원균에 의한 중금속 불용화를 보여주는 도면

도 6은 본 발명에 따른 소각재 처리방법의 제 1 실시예를 설명하기 위한 도면

도 7a부터 도 7d는 도 6에서 단위매립체의 종류를 설명하기 위한 도면

도 8a부터 도 8c는 본 발명에 따른 소각재 처리방법의 제 2 실시예를 설명하기 위한 도면

발명의 실시를 위한 최선의 형태 또는 발명의 실시를 위한 형태

이하에서는, 언급된 본 발명의 기술적 원리를 바탕으로 기존의 매립시설 구조에 황산염환원균을 이용하기 위하여 매립물의 상호보완적 특성을 고려하여 합리적이며 계획적으로 매립하는 방법으로, 1차적으로는 유기물과 중금속을 동시에 제거하고 2차적으로는 중금속을 회수할 수 있는 새로운 매립방법을 실시예들을 통하여 설명하고자 한다.

도 6은 본 발명에 따른 소각재 처리방법의 제 1 실시예로 소각재 및 하수슬러지의 매립방법을 설명하기 위한 도면이다.

본 발명에 따른 소각재 처리방법의 제 1 실시예는 소각재 및 하수슬러지를 매립하고, 그 상부를 복토층으로 덮어서 형성되는 매립물 구조를 제공한다.

도면에 보인 바와 같이, 매립물 하단에는 차수막(61)과 침출수배제관로(62)가 설치되어 있고, 그 상부에 단위매립체(63)가 다수의 층을 이루도록 배열되어 있다. 각각의 단위매립체(63)는 복토층(64)에 덮혀 있도록 구성되어 있다.

단위매립체(63)는 도 7a부터 도 7d에 보인 바와 같이, 소각재 및 하수슬러지를 다양하게 적층 혹은, 혼합하는 방식을 통하여 구성할 수 있다.

도 7a에 보인 바와 같이, 하수슬러지(A)를 우선, 매립하고, 그 상부에 소각재(B)를 매립한 후에 복토층(64)을 덮거나; 도 7b에 보인 바와 같이,

하수슬러지와 소각재의 혼합한 혼합폐기물(A+B)을 매립한 후에 복토층(64)을 덮거나; 도 7c에 보인 바와 같이, 하수슬러지(A)를 우선 매립하고, 그 상부에 일반폐기물(C)과 소각재(B)를 순차적으로 매립한 후에 복토층(64)을 덮거나; 도 7d에 보인 바와 같이, 하수슬러지, 일반폐기물 및 소각재의 혼합한 혼합폐기물(A+B+C)을 매립한 후에 복토층(64)을 덮는 매립방식이다.

상술한 바와 같은 단위매립체(63)의 형성을 반복적으로 실시하여 소정의 크기를 갖는 매립물 구조를 완성한다. 매립물 구조의 최상단은 최종복토층(66)이 전면을 덮도록 구성한다. 미설명 도면부호(67)는 매립물 구조를 지지하는 제방을 나타낸 것이고, (68)은 우수배제용관을 나타낸다.

상술한 매립물 구조에서 매립 이외의 시설에 관한 사항은 일반적인 위생매립기준에 따른다.

단위매립체(63)에서는 언급한 바와 같이, 하수슬러지의 황산염환원균이 하수슬러지의 유기물을 이용하는 이화작용을 통하여 얻은 에너지로 소각재 내의 황산염(SO_4^{2-})을 황화물(S^{2-})로 생성시키고, 상기 소각재 내의 중금속과 결합시켜 불용화된 금속황화물로 고형화시킨다. 따라서, 소각재 내의 중금속은 단위매립체(63) 내에서 안정적인 금속황화물로 고형화시킨다. 따라서, 침출수등에 용출되는 경우가 거의 없기 때문에 소각재 내의 중금속을 불용화시켜 안정화할 수 있다.

이 때, 매립작업 중이거나, 매립작업 후에 하수슬러지 혹은 일반폐기물에서 나오는 여분의 침출수는 침출수배제관로(62)를 통하여 배수된다. 침출수배제관로(62)를 통하여 배수된 침출수는 별도의 경로 즉, 침출수집수정 및 반응시설을 통하여 처리되어 외부로 배출되거나, 다시 매립물에 침투하게 하는

작업을 통하여 침출수 재순환 경로를 거치게 하여 적응된 황산염환원균에 의한 소각재내의 중금속 불용화 및 유기물안정화효과를 더욱 증대시킬 수 있다.

도 8은 본 발명에 따른 소각재 처리방법의 제 2 실시예로 소각재 및 하수슬러지의 매립방법을 설명하기 위한 도면이다.

본 발명에 따른 소각재 처리방법의 제 2 실시예는 소각재와 일반폐기물, 하수슬러지를 각각 별도로 매립했을 경우에 여기서 발생되는 침출수를 황산염환원균을 이용하여 혐기성으로 처리하는 방식을 제공한다.

도 8a를 참조하면, 소각재를 매립한 지역에서 나오는 침출수(81)와 하수슬러지를 매립한 지역에서 나오는 침출수(82)를 하나의 반응시설(85)에 혼합한다. 이 때, 일반폐기물에서 나오는 침출수(83)에 존재하는 황산염환원균을 이용하기 위하여, 일반폐기물을 매립한 지역에서 나오는 침출수(83)도 추가로 혼합할 수 있다.

미설명 도면부호(86)는 반응시설(85)내에 있는 소각재 침출수와 하수슬러지 침출수와 일반폐기물 침출수의 혼합액을 나타낸다.

도 8b를 참조하면, 반응시설(85) 내의 혼합액(86)에서 소각재 침출수 내에 용존하는 중금속을 하수슬러지 침출수 내에 존재하는 황산염환원균이 불용성 금속황화물(87)로 침전시킨다. 이 반응은 이미 언급한 바와 같다.

도 8c를 참조하면, 침전된 중금속(87)과 그 이외의 반응결과액(88)을 분리 배출하여 별도 관리한다. 이 때, 침전된 중금속은 별도의 중금속 회수시설(89)을 거쳐서 회수하는 것이 가능하기 때문에 자원활용면에서 잇점이 있다. 또한, 반응결과액(88)에는 혐기성 조건에서 적응된 황산염환원균이 다량 존재하기 때문에 소각재 처리방법에 재사용할 수 있다.

산업상 이용가능성

본 발명은 황산염환원균에 의하여 소각재의 중금속을 안전한 금속황화물로 침전시켜 불용화시킬 수 있으며, 그 결과로 소각재를 처리함에 있어서 중금속의 용출로 인한 주변의 토양 및 수질 오염의 가능성을 획기적으로 줄일 수 있다.

또한, 본 발명은 황산염환원균원으로 황산염환원균을 포함하는 유기성 폐기물 예를 들어, 하수슬러지를 사용할 경우에는 슬러지의 중금속 또한 처리할 수 있는 상승효과도 기대할 수 있다. 또한, 황산염환원균 뿐만 아니라 폐기물 슬러지에 존재하는 다른 종류의 균에 의하여 소각재 내의 중금속 제거율을 상승시킬 수 있다. 또한, 황산염환원균의 활발한 대사작용으로 인하여 하수 슬러지의 안정화를 효과적으로 상승시킬 수 있다.

본 발명은 기존 매립시설 구조에 황산염환원균을 이용하기 위하여 매립물의 상호보완적 특성을 고려하여 합리적이며 계획적으로 매립하는 방법 즉, 소각재의 중금속을 안정한 금속황화물로 불용화시키며 유기물도 동시 안정화시킴으로써, 다량 발생하는 소각재 및 하수슬러지의 처리·처분에 따른 문제점을 획기적으로 해결할 수 있다.

또한, 종래 기술이 소각재와 같은 유해폐기물과 일반 폐기물(유기성 폐기물 포함)을 분리하여 별개의 매립지에 매립 및 처리하기 때문에 매립지 확보에 어려움이 있고 처리비용이 많이 드는 데 반하여, 본 발명은 소각재도 일반 폐기물과 함께 매립하는 방식으로 소각재를 처리하기 때문에 매립지 확보면에서 유리하며, 소각재 및 폐기물 처리에 있어서 고비용을 요구하지 않는다는 장점이 있다.

본 발명은 제시된 실시예 뿐만이 아니라, 첨부된 특허청구범위 및 언급한 상술부분을 통하여 다양한 실시예로 구현될 수 있으며, 동업자에 의하여 다양한 방식으로 적용될 수 있다.

청구의 범위

1. 중금속을 함유하는 소각재 및 폐수 슬러지와 황산염환원균을 포함하는 유기성 폐기물과의 상호보완적 특성을 이용하여 상기 소각재와 상기 유기성 폐기물을 함께 매립하여, 상기 황산염 환원균으로 상기 소각재 내에 존재하는 황산염을 환원시켜 황화물을 생성시켜 상기 생성된 황화물을 상기 소각재 내에 존재하는 중금속과 결합시켜 불용성 금속황화물을 형성하여 상기 소각재로부터 중금속이 외부로 용출되지 않도록 하는 소각재 및 폐수슬러지 처리방법.

2. 청구항 1에 있어서.

상기 황산염환원균이 존재하는 하수슬러지를 포함하는 유기성 폐기물인 것이 특징인 소각재 및 폐수슬러지 처리 방법.

3. 소각재 내의 중금속을 황산염환원균이 불용성 금속황화물로 침전시켜 상기 소각재로부터 중금속이 외부로 용출되지 않도록 소각재 및 황산염환원균을 포함하는 유기성 폐기물을 함께 매립하고 복토를 덮어 매립물을 형성하는 소각재 및 폐수슬러지 처리방법.

4. 청구항 3에 있어서,

상기 소각재 및 황산염환원균을 포함하는 유기성 폐기물을 함께 매립하여 이루어진 매립체를 단위매립체로 하여 상기 단위매립체를 다수개로 형성하되, 소정의 배열방식으로 배열되도록 구성하고, 상기 단위매립체 들간에는 상기

복토층이 경계를 두게 하도록 매립물을 구성하는 소각재 및 폐수슬러지 처리방법.

5. 청구항 3 또는, 청구항 4에 있어서,

상기 황산염환원균이 존재하는 하수슬러지를 포함하는 유기성 폐기물인 것이 특징인 소각재 및 폐수슬러지 처리 방법.

6. 소각재를 매립한 지역에서 나오는 침출수와 황산염환원균을 포함하는 유기성 폐기물에서 나오는 침출수를 하나의 반응시설에 혼합하고 반응시켜, 상기 소각재 침출수 내에 용존하는 중금속을 상기 유기성 폐기물 침출수 내에 존재하는 황산염환원균이 불용성 금속황화물로 침전시켜 소각재의 침출수와 유기성 폐기물의 침출수를 처리하도록 구성되는 소각재 및 폐수슬러지 처리방법.

7. 청구항 6에 있어서,

상기 침전된 불용성 금속황화물을 상기 반응시설에서 추출하여 별도의 반응을 거쳐 소정의 중금속만을 회수하여 자원재활용하는 소각재 및 폐수슬러지 처리방법.

8. 청구항 6에 있어서,

상기 황산염환원균이 존재하는 하수슬러지를 포함하는 유기성 폐기물인 것이 특징인 소각재 및 폐수슬러지 처리 방법.

요약서

본 발명은 중금속을 함유하는 소각재 및 폐수슬러지 처리 시에 황산염환원균을 이용하기 위하여, 기존의 매립시설 구조에 매립물의 상호보완적 특성을 고려하여 합리적이며 계획적으로 매립하여 소각재의 중금속을 불용화시키고 유기물의 안정화를 유도하는 소각재 및 폐수슬러지 처리방법에 관한 것으로, 소각재에 황산염환원균을 포함하는 유기성 폐기물을 함께 매립하여 상기 황산염 황원균이 상기 소각재 내의 황산염을 환원시켜 그 결과로 생성된 황화물을 상기 소각재 내의 중금속과 결합시켜 불용성 금속황화물로 침전시키도록 구성되는 소각재 처리방법과 소각재 내의 중금속을 황산염환원균이 불용성 금속황화물로 침전시키도록 소각재 및 황산염환원균을 포함하는 유기성 폐기물을 함께 매립하고 복토를 덮어 매립물을 형성하는 소각재 처리방법을 제공하며, 황산염환원균에 의하여 소각재의 중금속을 안전한 금속황화물로 침전시켜 고형화시킬 수 있으며, 그 결과로 소각재를 처리함에 있어서 중금속의 용출로 인한 주변의 토양 및 수질 오염의 가능성을 획기적으로 줄일 수 있다.